Parameters affecting Accuracy and Reproducibility of Sedimentary Particle Size Analysis of Clays

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DECLARATION OF AUTHENTICITY

I, the undersigned, hereby declare that the work contained in this thesis is my own original work. It has not been previously, in its entirety, or in part, submitted at any University for a degree.

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ABSTRACT

The main aim of this study is to establish a standard procedure for all sedimentary particle size analysis methods specifically for clay minerals and mixtures thereof. Not only will it improve accuracy and reproducibility during clay size analysis, it will also secure comparability between different operators.

As a start, all the apparatus-related parameters that can affect the accuracy and reproducibility were determined for the apparatus used, *viz.* the Sedigraph 5000D. Thereafter, these parameters were kept constant, and the effects of potential material-related parameters were investigated one-by-one. First to be investigated were those parameters relating specifically to sample preparation. They were: grinding intensity, chemical dissolution of cementing materials, duration of prior soaking, salt content, centrifugal washing with polar organic liquids, deflocculant type and concentration, the effect of pH, ultrasonic time, and stirring during ultrasonic treatment.

Then, the influence on accuracy and reproducibility of the physical and chemical parameters related to the suspension was determined. They were: the use of the viscosity and density of water to calibrate the apparatus in stead of those of the suspension liquid, hydrolysis of the deflocculant with suspension-ageing, and the effect of solid concentration on hindered settling. During this investigation a novel method was developed to enable faster and more accurate pycnometric density determinations.

Next, the unique characteristics of clays, which can influence the results of sedimentary particle size analyses, were examined. Serious problems are encountered with the accuracy of the analyses of some clay types abundantly found in nature, *viz.* the smectites and mixed-layered clay minerals. Due to their swelling in water, and variations in the amounts of their crystal layers, they experience unpredictable changes in particle size. The latter is caused by the following external factors: clay type, humidity, type of exchange cation, electrolyte concentration, clay concentration, pH, deflocculant type and concentration, pressure history of the swell-clay suspension, and ageing of the suspension. The effect of each of them on the accuracy and reproducibility of the sedimentary particle size analysis of clays are investigated in detail.

Another problem that influences the accuracy of the sedimentary methods is that owing to

swelling, the densities of smectites and mixed-layered clays change by varying degrees when suspended in water. It is, however, impossible to pycnometrically determine the density of a swell-clay since it absorbs a part of the water used for its volume determination. To solve this problem, a novel method was devised to calculate swell-clay density. This method makes use of existing Monte Carlo simulations of the swelling mechanism of montmorillonite.

During all sedimentary methods, an average clay density is normally used to calculate the particle size distribution of clay mixtures. However, if there is a large enough difference between the calculated average density and that of a component, then inaccurate results will be recorded. The magnitude of this effect was investigated for a few self-made clay mixtures, which consisted of different proportions of kaolinite, illite, and montmorillonite.

Based on all the above results, a practical approach to, and a standard methodology for all the sedimentary methods of particle size analysis of clay minerals are presented. Additionally, a condensed summary is provided in table-form, which contains the magnitudes of the errors associated with each of the parameters that were examined.

OPSOMMING

Die doel van hierdie studie is om 'n standaard prosedure daar te stel vir alle sedimentêre metodes van partikelgrootte analise, spesifiek vir gebruik met kleiminerale en mengsels daarvan. So 'n standaard prosedure sal die akkuraatheid en herhaalbaarheid van klei-analises verbeter, en die vergelykbaarheid tussen verskillende operateurs verseker.

Aanvanklik is slegs die parameters bepaal wat die akkuraatheid en herhaalbaarheid van die gekose apparaat (Sedigraph 5000D) kan beïnvloed. Daarna is al hierdie parameters konstant gehou, en is die potensiële effekte van die moontlike materiaal-verwante parameters een na die ander ondersoek. Eerstens is die invloed van monstervoorbereiding op akkuraatheid en herhaalbaarheid bepaal. Verskillende parameters nl. maal-intensiteit, chemiese oplossing van sementerende materiale, sentrifugale wassing met polêre organiese vloeistowwe, tipe ontvlokker en konsentrasie, die effek van pH, ultrasoniese tyd en die effek van roer tydens ultrasonikasie is ondersoek.

Vervolgens is die invloed op die akkuraatheid en herhaalbaarheid van die fisiese en chemiese parameters verwant aan die suspensie bepaal. Hierdie parameters was nl. die gebruik van die viskositeit en digtheid van water in plaas van dié van die suspensievloeistof, hidrolise van die ontvlokker tydens suspensieveroudering, asook die effek van vastestof-konsentrasie op belemmerde uitsakking. Gedurende hierdie ondersoek is ook 'n nuwe metode ontwikkel wat vinniger, en meer akkurate piknometriese digtheidsbepalings moontlik maak.

Die unieke eienskappe van kleie wat die resultate van sedimentêre metodes van partikelgrootte analises kan beïnvloed, is volgende ondersoek. Tydens die analises van party kleie wat baie volop in die natuur voorkom, nl. die smektiete en menglaag-kleie, word ernstige akkuraatheids-probleme ondervind. Hul swelling in water, tesame met variasies in hul aantal kristal-lagies, veroorsaak onvoorspelbare verandering van hul partikelgroottes. Laasgenoemde word deur die volgende eksterne faktore veroorsaak: klei tipe, humiditeit, tipe uitruil-katioon, elektrolietkonsentrasie, kleikonsentrasie, pH, ontvlokker-tipe en konsentrasie, drukgeskiedenis van 'n swelklei-suspensie, en veroudering van die suspensie. Die effek van elk op die akkuraatheid en herhaalbaarheid van die sedimentêre partikelgrootte analises van kleie word in detail bespreek.

'n Verdere probleem wat die akkuraatheid van sedimentêre metodes beïnvloed, is dat

wanneer smektiete en menglaag-kleie in water gesuspendeer word, hulle digthede in verskillende mates weens swelling verander. Dit is egter onmoontlik om die digtheid van swelkleie in water piknometries te bepaal, omdat swelklei 'n gedeelte van die water absorbeer wat gebruik moet word om die kleivolume mee te bepaal. Om hierdie probleem op te los, is 'n nuwe metode ontwikkel om die digtheid van swelkleie mee te bereken. Die metode maak gebruik van reeds-bestaande Monte Carlo simulasies van die swelling van montmorillonite.

Tydens alle sedimentêre metodes word normaalweg van 'n gemiddelde kleidigtheid gebruik gemaak om die partikelgrootte-verspreiding van kleimengsels mee te bereken. Indien die berekende gemiddelde digtheid egter genoegsaam met dié van 'n kleikomponent verskil, sal onakkurate resultate verkry word. Hierdie effek is ondersoek vir 'n paar selfgemaakte kleimengsels wat uit verskillende hoeveelhede kaoliniet, illiet, en montmorilloniet bestaan het.

Laastens word 'n praktiese benadering en 'n standaard metode vir alle sedimentêre metodes voorgestel, wat gebaseer is op al die bogenoemde resultate. 'n Verkorte opsomming, met die groottes van die foute geassosieer met elke parameter wat ondersoek is, word laastens in tabelvorm verskaf.

TABLE OF CONTENTS

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1. INTRODUCTION

The gravitational sedimentary method of particle size analysis provides particle sizes that are obtained by the same process that controls sedimentation in nature. A size distribution determined in this way can therefore be used in calculations to characterise the hydrodynamic behaviour of sediments in natural waters. Sedimentary particle size analysis is therefore the preferred method for analysing very fine-grained, unconsolidated sediments. According to a survey conducted by Coates and Hulse (1985), it is also the standard method for clays in the field of soil science, as well as in the clay and ceramic industries. This method provides particle diameters ranging from the fine clay to the coarse silt size fractions.

1.1 AIM OF THE STUDY

Clay minerals have unique features that set them apart from all other mineral particles. Some of these features can affect the accuracy and reproducibility of all sedimentary methods of particle size analysis. Yet, no authoritative standard procedure, tailored specifically for clays, is currently available for this method of particle size analysis. Many of the sample-related parameters unique to clay minerals are not taken into account by the current standards for sedimentary methods[1].

The aim of this study is therefore to determine all sample-related parameters of clay minerals and clay mixtures (*i.e.* soils) that can affect the accuracy and reproducibility during all sedimentary methods. The application of the information obtained, is to present a standard procedure for sedimentary particle size analysis, tailored specifically for single clay minerals and clay mixtures (*e.g.* in soils). This will secure a means of comparability between the results of the same operator, as well as with that of other operators.

During the identification of all sample-related parameters, every possible apparatus-related parameter was identified beforehand and kept constant. Hence, the proposed standard

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[1] *British Standards (ISO 11277:1998, ISO 13317-1:2001, ISO 13317-2:2001, ISO 13317-3:2001, ISO 13318-1:2001, ISO 13318-2:2001),*

International Standards Organisation (BS ISO 13317-2:2001, BS ISO 13317-2:2001, BS ISO 13317-3:2001),

ASTM International Standards (B761-02, B761-89, D422-63(2002), D3360-96)

Gee and Bauder (1986).

procedure is related only to sample parameters, and therefore tailored for use with all methods of sedimentary particle size analysis of clays.

1.2 METHODOLOGY

During this study, the Sedigraph 5000D was used as apparatus of choice, firstly because it is widely used in the clay and paper industries. Like the Andreasen pipette method, the sedimentation balance, the hydrometer, and air classification, the Sedigraph also makes use of the sedimentation method of particle size analysis under gravitational force (Allen, 1995).

The Sedigraph furthermore gives much faster analysis times than for instance the Andreasen pipette method. For the average silicate with density 2.65 g/cm^3, an Andreasen Pipette with sedimentation depth 15 cm can take up to 10½ hr. to analyse down to 2 μm at 25 °C. However, under the same conditions, the Sedigraph will complete an analysis within only 12-13 min. Therefore, time-wise, the Sedigraph was also the obvious choice from amongst all the gravitational sedimentary methods of particle size analysis.

1.3 SCOPE OF THE STUDY

The method of operation of the Sedigraph 5000D, and the principles behind the sedimentation method of particle size analysis are provided in the next section. Thereafter, is presented a literature study on the unique characteristics of clay minerals affecting the accuracy and reproducibility of all sedimentary methods.

In Chapter 2, the reasons are given for choosing each one the three types of clay minerals used during this study (kaolinite, illite and montmorillonite). Then, the apparatus-related parameters of the Sedigraph 5000D, and the procedures to keep them in check during all analyses, are given in Chapter 3. In Chapters 4 to 6 are presented the experimental investigations to find the magnitudes of the effects of each sample-related parameter. Investigations were conducted on the following subjects: sample preparation procedures (section 4.1), the chemical and physical properties of clay suspensions (section 4.2), and the detrimental effects of swell-clays (Chapter 5).

The last chapter, Chapter 6, gives a summary of the literature and experimental investigations of each sample-related parameter, and the most important conclusions related to each. Based on this, a standard method for the sedimentary particle size analysis of clays is presented. Since the literature study and the experimental investigations provide a vast amount

of information, the reader is advised to first read the summary and conclusions contained in the last chapter. If more information on any subject or conclusion is required, the reader can use the provided cross-references to the relevant sections to acquire more detail. If a cross reference is not provided, the table of content can be used for this purpose.

A myriad of physical and chemical conditions govern the amount of swelling and the amount of unit-layers of swell-clays, and therefore also their particle sizes. In most cases the magnitudes of many of these conditions in the natural environment is either unknown, or they cannot be reproduced during sedimentary particle size analyses in water. Hence, also provided in the last chapter is an evaluation of the practice to use the particle size analyses of swell-clays to characterize their natural environments.

In conclusion, a summary in table-form is presented of the magnitude of the effect of each sample-related parameter on the accuracy and reproducibility of sedimentary particle size analysis.

The CD disk on the back-cover contains an MS Word soft-copy of this document (*Tesis2.doc*), along with a soft-copy of the report on the experimental determination of the apparatus parameters (*ApparatusParameters.doc* — see section 3.1)

1.4 THE SEDIGRAPH 5000D AND ITS PRINCIPLE OF OPERATION

To understand the principle of sedimentary particle size analysis, a brief explanation of the theory behind it, and a description of the Sedigraph 5000D itself and its method of operation, are provided below.

1.4.1 Sedimentation theory

With the sedimentary methods, the size of a particle, of any irregular shape, is derived from its settling velocities in a liquid. Determined by this method, the particle size is called the *equivalent spherical diameter* (esd). The esd of an irregular particle is defined as the diameter of a perfect sphere of same density, which settles at the same terminal settling velocity, under similar conditions (Allen, 1995).

When a particle settles in a liquid it experiences a downward gravitational force, which is countered by two upwards acting forces *viz.* buoyancy force, and drag force. The latter is proportional to the settling velocity. Therefore, after settling starts, the fall velocity increases, which a simultaneous increase in the opposing drag force. Soon the downward gravitational

force is equal to the upward buoyancy force plus drag force, and the particle reaches a constant terminal velocity.

The larger and denser a particle, the larger is its terminal settling velocity. To calculate the esd (or Stokes diameter) the relationship between particle size, density, liquid properties, and terminal settling velocity is used. The exact relationship between these entities is defined in the following equation, called Stokes' Law (Stokes, 1901):

$$D_{St} = \sqrt{\frac{18\eta u_{St}}{(\rho_s - \rho_f)g}} \qquad \text{Eq. 1.4.1.1}$$

D_{St} is the esd of the sphere (cm), η is the viscosity of the fluid (poises), u_{St} is the terminal settling velocity of the sphere in the laminar flow region (cm/sec.), ρ_s and ρ_f are the densities of the solid and the liquid (g/cm^3), respectively, and g is the gravitational constant (approximately 981 cm/sec.^{2}).

By rearranging Eq. 1.4.1.1 the working-forms of Stokes' Law in terms of settling time is obtained as follows:

$$u_{St} = \frac{g(\rho_s - \rho_f)D_{St}^{\ 2}}{18\eta} = K_{St1}D_{St}^{\ 2} \qquad \text{Eq. 1.4.1.2}$$

with:
$$K_{St1} = \frac{g(\rho_s - \rho_f)}{18\eta} \qquad \text{Eq. 1.4.1.3}$$

But since $u_{St} = h/t$ (were h is the sedimentation depth in cm, and t is the settling time in seconds) one can obtain the sedimentation time for any chosen particle size at any chosen sedimentation depth by re-arranging Eq. 1.4.1.2 as follows:

$$t = \frac{18\eta h}{g(\rho_s - \rho_f)D_{St}^{\ 2}} = \frac{K_{St2}h}{D_{St}^{\ 2}} \qquad \text{Eq. 1.4.1.4}$$

with:
$$K_{St2} = \frac{18\eta}{g(\rho_s - \rho_f)} \qquad \text{Eq. 1.4.1.5}$$

which is the first working-form of Stokes' Law.

Re-arranging Eq. 1.4.1.4 gives the second working-form of Stokes' Law, by which to calculate the Stokes' diameter (esd) at depth h after a settling time t:

$$D_{St} = \sqrt{\frac{K_{St2}h}{t}} \qquad \text{Eq. 1.4.1.6}$$

Eq. 1.4.1.6 is used to calculate particle size (esd) during all the sedimentary methods.

The results of all sedimentation methods are given as the cumulative mass percentage (cmp) below the calculated esd – also called cumulative mass percentage undersize. Stated differently: the cmp is the mass percentage of all particles smaller than a calculated particle size (expressed as a percentage of the total mass of all particles).

The next two sections describe the apparatus and methodology by which the Sedigraph determines the cmp below the calculated esd.

1.4.2 General description of the apparatus

Unless stated otherwise, this description of the Sedigraph is a concise summary of parts of the Sedigraph 5000D Instruction Manual (1979).

The Sedigraph 5000D particle size analyser directly determines the cmps (cumulative mass percentages) below decreasing particles sizes. To achieve this, the cmp is measured continually, while scanning the sample cell downwards past a stationary X-ray beam. Therefore in practical terms: the beam scans the cell from bottom to top.

To continuously be able to determine the cmp at the correct particle sizes, the cell is scanned at a rate that changes according to a hyperbolic function of depth vs. time, derived directly from Stokes' Law. The Sedigraph continuously presents its data as a graph of the cmp of all particles smaller than the particle size being recorded. Being calculated by means of Stokes' Law, particle size is expressed as equivalent spherical diameter. The reason for scanning is that it reduces the analysis time by a factor of about 2x as compared to the Andreasen pipette method.

Since the Andreasen method extracts large amounts of suspension, it requires a much deeper suspension column than the Sedigraph to prevent disturbing it (30 cm, or more). With the Sedigraph, no suspension is extracted or disturbed (Svarovsky and Allen, 1970). A very fine X-ray beam is used to determine the cmp, which requires a much smaller sedimentation height (3.5 cm). Along with scanning, the small sedimentation height of the Sedigraph sample cell further adds to its fast analysis time. At 25 °C, it takes the Sedigraph only 13 min. to analyse down to 2 µm, where it can take up to 10 ½ hours with the Andreasen pipette.

Moreover, to complete an analysis to 0.1 µm, it takes 30 full days with the Andreasen pipette; the Sedigraph does the same in only 5 h (Weaver and Grobler, 1981). Added to that, pipette samples need to be dried overnight before weighing them, and calculating the results.

The Sedigraph's X-ray tube is situated to the left of its sample cell (Fig. 1.4.2.1). The X-ray beam is collimated through a collimator slit to a height of 0.05 mm, and a width of 9.5 mm. The collimator is also situated to the left, but right next to the sample cell. The collimated X-ray beam transmits through the cell's transparent homolite plastic windows, and through the sample suspension, to a scintillation counter detector situated on the right-hand side of the sample cell. The cell, clipped into a cell holder, is moved downwards by means of a computer controlled stepper motor.

In order to calibrate the Sedigraph to accurately measure the cmp, the first step is to adjust the 0% setting while the cell is filled with clear suspension liquid. This adjustment determines the X-ray intensity while transmitting through the combination of the suspension liquid and cell windows – *i.e.* it acquires the X-ray intensity should 0% clay be present in the measuring zone of the X-ray beam within the cell.

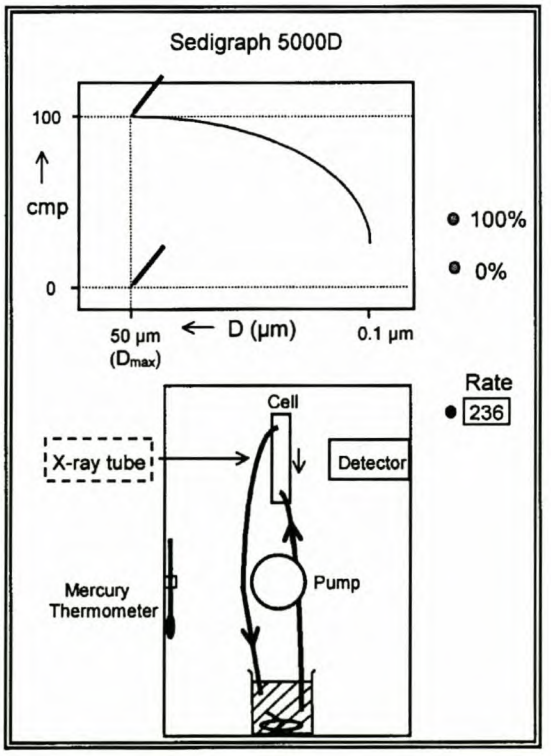

Fig. 1.4.2.1. Schematic representation of the Sedigraph 5000D

While the cell is still only filled with suspension liquid, the proper positioning of the graph on the graph paper is partially ensured by adjusting of the recorder pen on the 0% cmp line of the graph paper (this is called zeroing the pen).

The sample is beforehand dispersed in water plus chemical deflocculant, contained in a 100 cm^3 Pyrex beaker. This is now placed on a magnetic stirrer in the sample compartment (Fig. 1.4.2.1). While continuously being stirred to insure homogeneity, the suspension is then pumped through the sample cell, and the 100% setting is adjusted. This time the apparatus is calibrated to the X-ray intensity at the specific concentration of the sample suspension – *i.e.* the X-ray intensity registered when all particle sizes are represented in the measuring zone at 100% their concentrations in the dry sample. From the X-ray intensity through the sample suspension the Sedigraph now can calculate the cmp.

The positioning of the graph is completed during the 100% adjustment, by moving the pen to where the horizontal 100% cmp line intersects the vertical line of the largest particle size estimated for the sample (D_{max}) (Fig. 1.4.2.1). When moving the pen, the X-ray beam is simultaneously positioned at the suspension depth of the measuring zone where the cmp of the maximum particle size (D_{max}) will be measured at the start of the recording. After the zeroing, 0% and 100% adjustments are completed, the recorder is also synchronised exactly with the cell scan speed.

When the start switch is selected, the pump automatically stops. By using the adjusted cell scan rate, the Sedigraph computer calculates the length of the waiting period for the largest particles (D_{max}) to reach the measuring zone from the top of the suspension. After expiry of the waiting period, the stepper motor automatically starts the analysis by scanning the cell downwards past the X-ray beam, while the pen starts recording at the chosen D_{max} value.

When the analysis starts, the pen records the same esd on the graph paper as the actual particle size simultaneously reaching the X-ray beam from the top of the cell. This is continuously achieved by calculating with Stokes' Law the distance travelled by every particle size according to the elapsed analysis time. The Sedigraph computer then synchronises both the rate of pen movement and the sample scan rate to correctly record the esd at every sample depth. The graph is presented logarithmically on three-cycle, semi-log graph paper. A particle size distribution determined by the Sedigraph 5000D can range between 100 µm and 0.1 µm.

To achieve this synchronisation that assures the appropriate speed of travel for both the cell and pen in relation to the terminal settling velocity of increasingly smaller particles, the Sedigraph uses an adapted form of Stokes' Law to calculate its cell scan rate. Apart from the

particle density, and the density and viscosity of the suspension liquid, this equation also incorporates the starting diameter (the estimated largest particle size in the sample, D_{max}) and the power line frequency:

$$Cell\ \ scan\ \ rate = \frac{211.8\ \left(\rho_s - \rho_f\right)}{\left(50Hz / D_{\max}\right)^2 \eta} \times \frac{60}{Power\ \ line\ \ frequency} \qquad \text{Eq. 1.4.2.1}$$

The power line frequency in South Africa is 50 cycles per second. Densities are given in g/cm^3, and the viscosity (η) in c. poise. The D_{max} needs to be estimated for each sample before its analysis. The larger the D_{max} is chosen, the higher the scan rate, and therefore the shorter the analysis time.

Using the adjusted cell scan rate, the rate of movement of the recorder and the sample cell is electronically adapted to the viscosity and density of the sedimentation liquid at the analysis temperature. Additionally, through the chosen D_{max}, the rate of movement of the recorder and the sample cell is adapted to the expected width of the particle size distribution: the wider the particle size distribution, the faster both recorder and cell must move at the start of the analysis to keep up with the rate of particle movement. To take into account any change in temperature since the last analysis, the scan rate of the sample cell is always recalculated before the next one. Due to all the above measures, the particle sizes recorded on the graph paper are the same as the actual particle sizes in the detection zone within the cell.

Scanning upwards, the X-ray beam will encounter smaller and smaller particles, since the larger and faster moving particles had already passed the upwards-moving measuring zone. As a result, the X-ray beam simultaneously encounters fewer particles; hence, the concentration (cmp) decreases as particle size decreases.

To determine the cmp at each particle size, the amount of X-rays absorbed by the sample is continuously calculated at increasingly lower depth in the sample cell. This is accomplished by comparing the transmitted X-ray intensity at any given moment to that when the suspension was pumped through the cell during the 100% adjustment. After that, by using the intensity when the cell is filled only with suspension liquid (registered during the 0% adjustment), the amount of X-rays absorbed by the suspension is recalculated to cmp (for the method of calculation see the Instruction Manual Sedigraph 5000D, 1979). Due to the above-mentioned synchronization of cell, pen, and particle movement, the cmp is continuously presented against the true particle size on the x-y recorder.

By using Eq. 1.4.2.1 the cell scan rates for the expected range of operational temperatures of the Sedigraph (from 20 ºC to 40 ºC) was calculated (Table 1.4.2.1). This table was used to adjust the correct scan rate before, and during each analysis of this study.

Table 1.4.2.1. Sedigraph 5000D sample scan rate for kaolin suspensions calculated at temperatures between 20 −40 °C (in steps of 0.1 °C), and for the chosen D_{max} of either 30μ, 40μ, 50μ or 65μ.

MEASURED TEMPERATURE (°C)	CALCULATED		CALCULATED RATE				MEASURED TEMPERATURE (°C)	CALCULATED		CALCULATED RATE			
	DENSITY (g/cc)	VISCOSITY (C.Poise)	D-Max. 30 μm	D-Max. 40 μm	D-Max. 50 μm	D-Max. 65 μm		DENSITY (g/cc)	VISCOSITY (C.Poise)	D-Max. 30 μm	D-Max. 40 μm	D-Max. 50 μm	D-Max. 65 μm
20.0	0.9982075	0.9980	150	266	416	702	25.1	0.9970226	0.8849	169	300	469	793
20.1	0.9981868	0.9956	150	267	417	704	25.2	0.9969968	0.8829	169	301	470	794
20.2	0.9981660	0.9931	150	267	418	706	25.3	0.9969709	0.8809	170	302	471	796
20.3	0.9981451	0.9907	151	268	419	707	25.4	0.9969449	0.8789	170	302	472	798
20.4	0.9981241	0.9883	151	269	420	709	25.5	0.9969189	0.8769	170	303	473	800
20.5	0.9981030	0.9859	151	269	421	711	25.6	0.9968927	0.8749	171	304	474	802
20.6	0.9980818	0.9835	152	270	422	713	25.7	0.9968664	0.8730	171	304	475	804
20.7	0.9980605	0.9812	152	271	423	714	25.8	0.9968401	0.8710	172	305	477	805
20.8	0.9980390	0.9788	153	271	424	716	25.9	0.9968136	0.8690	172	306	478	807
20.9	0.9980175	0.9764	153	272	425	718	26.0	0.9967871	0.8671	172	306	479	809
21.0	0.9979959	0.9741	153	273	426	720	26.1	0.9967605	0.8651	173	307	480	811
21.1	0.9979742	0.9717	154	273	427	721	26.2	0.9967337	0.8632	173	308	481	813
21.2	0.9979523	0.9694	154	274	428	723	26.3	0.9967069	0.8613	174	308	482	815
21.3	0.9979304	0.9671	154	275	429	725	26.4	0.9966800	0.8593	174	309	483	816
21.4	0.9979083	0.9648	155	275	430	727	26.5	0.9966530	0.8574	174	310	484	818
21.5	0.9978862	0.9624	155	276	431	728	26.6	0.9966259	0.8555	175	311	485	820
21.6	0.9978639	0.9601	156	277	432	730	26.7	0.9965987	0.8536	175	311	486	822
21.7	0.9978416	0.9579	156	277	433	732	26.8	0.9965714	0.8517	175	312	487	824
21.8	0.9978191	0.9556	156	278	434	734	26.9	0.9965440	0.8498	176	313	489	826
21.9	0.9977966	0.9533	157	279	435	735	27.0	0.9965166	0.8479	176	313	490	827
22.0	0.9977739	0.9510	157	279	436	737	27.1	0.9964890	0.8461	177	314	491	829
22.1	0.9977512	0.9488	157	280	437	739	27.2	0.9964614	0.8442	177	315	492	831
22.2	0.9977283	0.9465	158	281	438	741	27.3	0.9964336	0.8423	177	315	493	833
22.3	0.9977054	0.9443	158	281	439	742	27.4	0.9964058	0.8405	178	316	494	835
22.4	0.9976823	0.9421	159	282	440	744	27.5	0.9963779	0.8386	178	317	495	837
22.5	0.9976592	0.9398	159	283	441	746	27.6	0.9963498	0.8368	179	318	496	839
22.6	0.9976359	0.9376	159	283	442	748	27.7	0.9963217	0.8349	179	318	497	840
22.7	0.9976126	0.9354	160	284	444	750	27.8	0.9962935	0.8331	179	319	498	842
22.8	0.9975891	0.9332	160	285	445	751	27.9	0.9962653	0.8313	180	320	500	844
22.9	0.9975655	0.9310	160	285	446	753	28.0	0.9962369	0.8295	180	320	501	846
23.0	0.9975419	0.9289	161	286	447	755	28.1	0.9962084	0.8276	181	321	502	848
23.1	0.9975181	0.9267	161	287	448	757	28.2	0.9961799	0.8258	181	322	503	850
23.2	0.9974943	0.9245	162	287	449	758	28.3	0.9961512	0.8240	181	323	504	852
23.3	0.9974703	0.9224	162	288	450	760	28.4	0.9961225	0.8222	182	323	505	854
23.4	0.9974463	0.9202	162	289	451	762	28.5	0.9960936	0.8205	182	324	506	855
23.5	0.9974221	0.9181	163	289	452	764	28.6	0.9960647	0.8187	183	325	507	857
23.6	0.9973979	0.9160	163	290	453	766	28.7	0.9960357	0.8169	183	325	508	859
23.7	0.9973736	0.9138	163	291	454	767	28.8	0.9960066	0.8151	183	326	509	861
23.8	0.9973491	0.9117	164	291	455	769	28.9	0.9959774	0.8134	184	327	511	863
23.9	0.9973246	0.9096	164	292	456	771	29.0	0.9959482	0.8116	184	327	512	865
24.0	0.9972999	0.9075	165	293	457	773	29.1	0.9959188	0.8099	185	328	513	867
24.1	0.9972752	0.9054	165	293	458	775	29.2	0.9958894	0.8081	185	329	514	869
24.2	0.9972504	0.9033	165	294	459	776	29.3	0.9958598	0.8064	185	330	515	870
24.3	0.9972255	0.9012	166	295	460	778	29.4	0.9958302	0.8047	186	330	516	872
24.4	0.9972004	0.8992	166	295	462	780	29.5	0.9958005	0.8029	186	331	517	874
24.5	0.9971753	0.8971	167	296	463	782	29.6	0.9957707	0.8012	187	332	518	876
24.6	0.9971501	0.8951	167	297	464	784	29.7	0.9957408	0.7995	187	332	520	878
24.7	0.9971248	0.8930	167	297	465	785	29.8	0.9957108	0.7978	187	333	521	880
24.8	0.9970994	0.8910	168	298	466	787	29.9	0.9956808	0.7961	188	334	522	882
24.9	0.9970739	0.8889	168	299	467	789	30.0	0.9956506	0.7944	188	335	523	884
25.0	0.9970483	0.8869	168	299	468	791							

Table 1.4.2.1 Continued

MEASURED TEMPERATURE (°C)	CALCULATED		CALCULATED RATE				MEASURED TEMPERATURE (°C)	CALCULATED		CALCULATED RATE			
	DENSITY (g/cc)	VISCOSITY (C.Poise)	D-Max. 30 µm	D-Max. 40 µm	D-Max. 50 µm	D-Max. 65 µm		DENSITY (g/cc)	VISCOSITY (C.Poise)	D-Max. 30 µm	D-Max. 40 µm	D-Max. 50 µm	D-Max. 65 µm
30.1	0.9956204	0.7927	189	335	524	886	35.1	0.9940008	0.7151	209	372	581	983
30.2	0.9955901	0.7910	189	336	525	887	35.2	0.9939663	0.7137	210	373	583	985
30.3	0.9955596	0.7894	189	337	526	889	35.3	0.9939317	0.7123	210	374	584	987
30.4	0.9955292	0.7877	190	338	527	891	35.4	0.9938971	0.7108	211	374	585	989
30.5	0.9954986	0.7860	190	338	529	893	35.5	0.9938624	0.7094	211	375	586	991
30.6	0.9954679	0.7844	191	339	530	895	35.6	0.9938276	0.7080	211	376	587	993
30.7	0.9954371	0.7827	191	340	531	897	35.7	0.9937927	0.7066	212	377	589	995
30.8	0.9954063	0.7810	191	340	532	899	35.8	0.9937577	0.7052	212	377	590	997
30.9	0.9953754	0.7794	192	341	533	901	35.9	0.9937227	0.7038	213	378	591	999
31.0	0.9953444	0.7778	192	342	534	903	36.0	0.9936876	0.7025	213	379	592	1001
31.1	0.9953133	0.7761	193	343	535	905	36.1	0.9936524	0.7011	214	380	593	1003
31.2	0.9952821	0.7745	193	343	536	907	36.2	0.9936171	0.6997	214	380	594	1005
31.3	0.9952508	0.7729	194	344	538	909	36.3	0.9935817	0.6983	214	381	596	1007
31.4	0.9952195	0.7713	194	345	539	910	36.4	0.9935463	0.6969	215	382	597	1009
31.5	0.9951880	0.7697	194	346	540	912	36.5	0.9935108	0.6956	215	383	598	1011
31.6	0.9951565	0.7681	195	346	541	914	36.6	0.9934752	0.6942	216	383	599	1013
31.7	0.9951249	0.7665	195	347	542	916	36.7	0.9934395	0.6929	216	384	600	1015
31.8	0.9950932	0.7649	196	348	543	918	36.8	0.9934037	0.6915	217	385	602	1017
31.9	0.9950614	0.7633	196	348	544	920	36.9	0.9933679	0.6902	217	386	603	1019
32.0	0.9950296	0.7617	196	349	546	922	37.0	0.9933320	0.6888	217	386	604	1021
32.1	0.9949976	0.7601	197	350	547	924	37.1	0.9932960	0.6875	218	387	605	1023
32.2	0.9949656	0.7585	197	351	548	926	37.2	0.9932599	0.6861	218	388	606	1025
32.3	0.9949335	0.7570	198	351	549	928	37.3	0.9932238	0.6848	219	389	607	1027
32.4	0.9949013	0.7554	198	352	550	930	37.4	0.9931876	0.6835	219	390	609	1029
32.5	0.9948690	0.7538	198	353	551	932	37.5	0.9931513	0.6821	220	390	610	1031
32.6	0.9948366	0.7523	199	354	552	934	37.6	0.9931149	0.6808	220	391	611	1033
32.7	0.9948042	0.7507	199	354	554	936	37.7	0.9930785	0.6795	220	392	612	1035
32.8	0.9947717	0.7492	200	355	555	938	37.8	0.9930419	0.6782	221	393	613	1037
32.9	0.9947390	0.7477	200	356	556	939	37.9	0.9930053	0.6769	221	393	615	1039
33.0	0.9947063	0.7461	201	357	557	941	38.0	0.9929687	0.6756	222	394	616	1041
33.1	0.9946736	0.7446	201	357	558	943	38.1	0.9929319	0.6743	222	395	617	1043
33.2	0.9946407	0.7431	201	358	559	945	38.2	0.9928951	0.6730	223	396	618	1045
33.3	0.9946078	0.7416	202	359	561	947	38.3	0.9928582	0.6717	223	396	619	1047
33.4	0.9945747	0.7401	202	359	562	949	38.4	0.9928212	0.6704	223	397	621	1049
33.5	0.9945416	0.7386	203	360	563	951	38.5	0.9927841	0.6691	224	398	622	1051
33.6	0.9945084	0.7370	203	361	564	953	38.6	0.9927470	0.6679	224	399	623	1053
33.7	0.9944752	0.7356	203	362	565	955	38.7	0.9927098	0.6666	225	400	624	1055
33.8	0.9944418	0.7341	204	362	566	957	38.8	0.9926725	0.6653	225	400	625	1057
33.9	0.9944084	0.7326	204	363	567	959	38.9	0.9926351	0.6641	226	401	627	1059
34.0	0.9943748	0.7311	205	364	569	961	39.0	0.9925976	0.6628	226	402	628	1061
34.1	0.9943412	0.7296	205	365	570	963	39.1	0.9925601	0.6615	226	403	629	1063
34.2	0.9943076	0.7281	206	365	571	965	39.2	0.9925225	0.6603	227	403	630	1065
34.3	0.9942738	0.7267	206	366	572	967	39.3	0.9924849	0.6590	227	404	632	1067
34.4	0.9942400	0.7252	206	367	573	969	39.4	0.9924471	0.6578	228	405	633	1069
34.5	0.9942060	0.7238	207	368	574	971	39.5	0.9924093	0.6565	228	406	634	1071
34.6	0.9941720	0.7223	207	368	576	973	39.6	0.9923714	0.6553	229	407	635	1073
34.7	0.9941379	0.7209	208	369	577	975	39.7	0.9923334	0.6541	229	407	636	1075
34.8	0.9941038	0.7194	208	370	578	977	39.8	0.9922954	0.6528	230	408	638	1078
34.9	0.9940695	0.7180	208	371	579	979	39.9	0.9922573	0.6516	230	409	639	1080
35.0	0.9940352	0.7165	209	371	580	981	40.0	0.9922191	0.6504	230	410	640	1082

1.4.3 The physical mechanism of sedimentary particle size analysis

The physical mechanism used to determine the cumulative mass percentage undersize during sedimentary particle size analysis is not adequately explained in the Sedigraph handbook, nor in the literature studied. Therefore, an explanation is provided below by using a Sedigraph analysis as an example.

Shortly after pumping stops – in the time-lapse before scanning commences – all turbulence comes to a rest. At that point, the suspension in the sample cell is homogeneous. Hence, the cmp below any given particle size is very close to equal in every point-volume of

the suspension. Accordingly, the cmp is very close to equal along any level in the suspension. Hence, the cmps below all particle sizes along any level in the suspension now represents their cmps in the homogenised dry powder sample.

All particles of (say) 20 µm along the roof of the cell at the start (BD – Fig. 1.4.3.1 (a)) will after settling time t_{20}, have moved through a sedimentation height of h_{20} to the measuring zone AF (Fig. 1.4.3.1 (b)). However, those particles *smaller* than 20 µm along the roof of the *cell* at the start will have settled slower during the same period, and therefore will still be above the measuring zone (DG). Simultaneously, all the particles *larger* than 20 µm along the roof (BC– Fig. 1.4.3.1 (a)) will have moved faster than the 20 µm particles to below the measuring zone, and will be situated between positions H and I (Fig. 1.4.3.1 (b)).

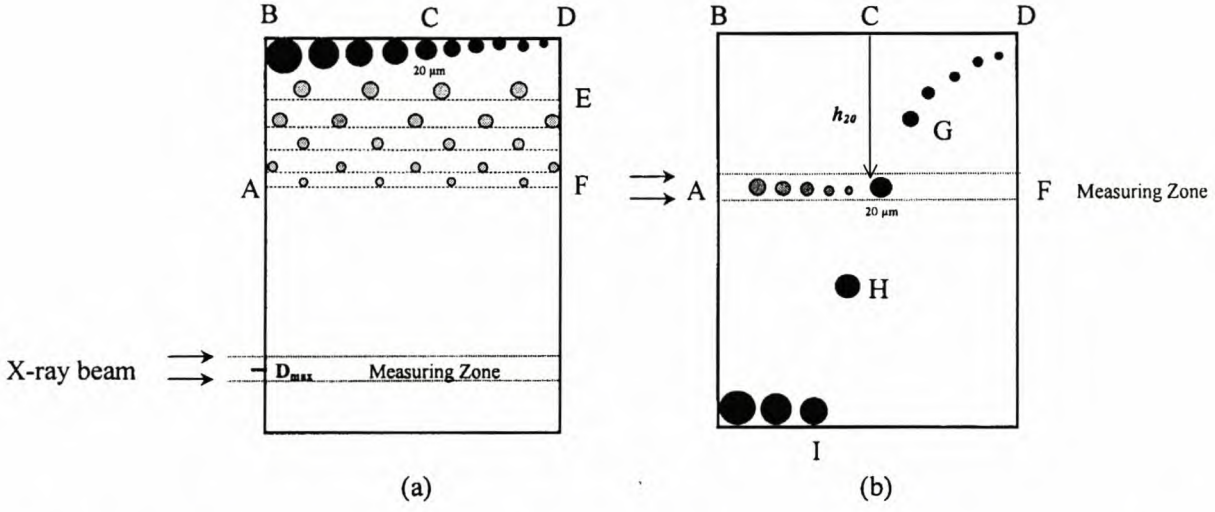

Fig. 1.4.3.1. Schematic drawings to explain the cumulative mass percent undersize principle by using the Sedigraph sample cell

At the start there will also be particles smaller than 20 µm, positioned along specific horizontal levels between positions E and F, that are at such particle sizes that they will also reach the measuring zone after the same settling time t_{20} (Fig. 1.4.3.1 (a)). But all particles along these levels *smaller* than the last-mentioned particles will still be above the measuring zone AF. In contrast, particles *larger* than that in the horizontal EF levels will, after settling time t_{20}, have passed the measuring zone (to simplify the drawings both the last two particle types are not shown). Hence, the measuring zone now only contains particles smaller than 20 µm. In the meantime, the X-ray beam had scanned upwards from the D_{max} position, to reach the measuring zone AF at exactly the same moment. Simultaneously on the plotter graph, the

pen had recorded up to the 20 μm particle size.

In terms of cmp the following picture emerges after time t_{20}: Since particles of the same size will move at the same velocity, every EF particle now in the measuring zone AF will be at the same relative amount (and hence the same cmp) as it had along their respective E–F horizontal levels at the start – which is the same cmp as it originally had in the dry powder sample. Since the measuring zone will now only contain particles smaller than 20 μm, the concentration at the measuring zone represents the cmp below 20 μm of the dry powder sample. The X-ray intensity is at the same instant converted to cmp, and registered on the plotter graph as being below 20 μm.

1.5 UNIQUE PROPERTIES OF CLAY MINERALS AFFECTING ACCURACY AND REPRODUCIBILITY

Clay particles have a number of features distinguishing them from other minerals in terms of their effect on accuracy and reproducibility during particle size analysis (some affecting only the sedimentary methods):

- Due to typically wide size distributions, large portions of clay samples may fall below the lower particle size limit for the sedimentary methods.
- The true dimensions of clay platelets differ vastly from the equivalent spherical diameter obtained by the sedimentary methods.
- When using the Sedigraph the low X-ray absorbancy of clay minerals necessitates high solid concentrations, which causes inaccuracy associated with hindered settling during sedimentary methods.
- The high surface charge and its dual nature, as well as the platy shape of clay particles, cause them to flocculate (stick together) in water more readily than other mineral particles. The straight surfaces of clay platelets should also contribute to the degree of flocculation.
- High surface charge also gives clay surfaces the ability to hydrolyse chemical dispersants. The result is flocculation, which compromises the accuracy of particle size analysis.
- Some sample preparation techniques can modify the particle size of individual clay minerals. Soil minerals often are bound into strong aggregates by secondary minerals

and organic material. The chemical methods needed to remove them, can reduce the particle size of clay particles in a number of ways. Furthermore, grinding of clay samples to facilitate weighing, may easily delaminate clay platelets along their well-developed {001} cleavages, reducing particle sizes. For the same reason swell-clays and mixed-layered clay minerals may also delaminate under ultrasonic treatment.

- Owing to the absorption of water between their crystal layers during particle size analysis, the smectites, vermiculite, and mixed-layered clay minerals decrease in density. For this reason their densities cannot be determined pycnometrically. Hence, when using any sedimentary method, the particle size of swell-clays cannot be calculated accurately.
- Various chemical and physical factors determine the extent of swelling, as well as the amount of unit-layers of some swell-clay particles. Furthermore, during any particle size analysis clay particles need to be deflocculated. However, in the presence of deflocculants some smectites collapse to a much smaller particle size. Others exfoliate completely into their separate unit-layers, resulting in even smaller particles.

The causes of each of the above attributes of clay minerals, and the reasons why each affects accuracy and reproducibility specifically during sedimentary methods, are discussed below.

1.5.1 Effect of the wide particle size distribution of clays

The particle size of clay minerals falls between the fine clay size-fraction (0.08 μm) to the upper margin of the coarse silt size-fraction (50 μm) (Jackson, 1968).

This wide size distribution of clay minerals presents a problem when using any sedimentary method. The sizes of the smallest clay particles fall below the lower size limit of 0.56 μm. However, the sizes of the largest clay particles coincide exactly with the *upper* size limit of 49.6 μm for the sedimentary methods.

In the next two sections the reasons why the sedimentary principle necessitates these size limits, as well as the formulae to calculate them, are discussed.

1.5.1.1 Calculating the upper and lower limits for sedimentary particle size analysis

The upper size limit for the sedimentary methods is necessitated by the breakdown of Stokes' Law, and by the turbulence of mixing during the first 30 seconds of an analysis (Allen,

1995). The lower size limit, on the other hand, is confined by the size of the effect of Brownian diffusion.

The turbulence of mixing refers to the continued turbulence in the sample cell just after the Sedigraph pump is switched off at the start of an analysis, or after the vessels of the other sedimentary methods have been agitated. This is followed by a period of waiting for the largest particles to reach the detection zone just before measuring starts. If the largest particles are too big, the period of waiting will be too short. Then a too large part of the settling distance of the largest particles will be during the last remainders of the turbulence of mixing. Consequently, inaccurate cmp values will be registered for them.

The next two sections deal with the causes of the breakdown of Stokes' Law and Brownian diffusion, their effects on accuracy and reproducibility, and the calculation of the upper and lower size limits for all sedimentary methods.

1.5.1.1.1 Turbulent flow and the upper size limit

A settling particle exerts an acceleration force on the static liquid through which it travels (Pettijohn *et al.*, 1972). Some liquid, consisting of a laminate of very thin water layers, is dragged along on the particle surface. The layer closest to the particle surface has the same velocity as the particle while, away from the surface, the layer-velocities rapidly decreases to zero. These layers of moving liquid are collectively called the boundary layer (Fig. 1.5.1.1.1.1).

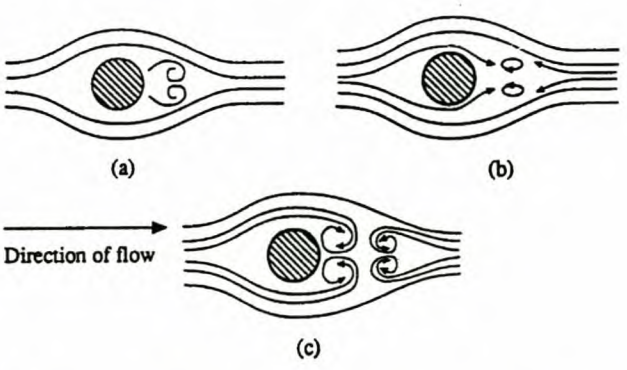

Fig. 1.5.1.1.1.1. Development of turbulent flow behind a moving particle (after Allen, 1995)

When a particle's size and density are small enough, its terminal settling velocity is slow enough to allow smooth flow between the liquid layers in the boundary layer. Such flow is called *laminar*, *streamline,* or *viscous flow* in the Stokes or *laminar flow regime* (Allen, 1995). Under such flow conditions, the esd can still be calculated with acceptable accuracy by means

of *Stokes' Law*; the esd is therefore called the *Stokes diameter*.

However, as diameters and/or densities increase, particles eventually have terminal settling velocities high enough that the boundary layer starts detaching itself, forming vortices behind the particle (Allen, 1995; Fig. 1.5.1.1.1.1 (a)). Vortices increase particle drag, and reduce the terminal settling velocity below that predicted by Stokes' Law. This is called the breakdown of Stokes' Law. It happens at the crossover point from the laminar flow regime to the *transitional flow regime*. With further increase in settling velocity, irregular particles start to rotate, resulting in even more drag. Hence, beyond the crossover point, the sedimentary methods slowly become more inaccurate.

The crossover point between the laminar and transitional flow regimes can be numerically defined by the Reynolds number (R_e), which is given by:

$$R_e = \frac{\rho_f u D}{\eta} \qquad \text{Eq. 1.5.1.1.1.1}$$

where ρ_f is the fluid density (g/cm^3), u the particle terminal settling velocity (cm/sec.), D the particle esd (cm), and η is the suspension-liquid viscosity (poises) (Allen, 1995). The cross-over point between laminar and transitional flow regimes is at a R_e of around 0.25.

With further increase in particle size and/or density, the vortices increase in size, and move further downstream (Fig. 1.5.1.1.1.1 (b)). For even large and denser particles with R_e between 0.25 and 1 the vortices break up to form new ones, and the wake becomes fully turbulent (Fig. 1.5.1.1.1.1 (c)). This is called the *turbulent* or *non-viscous flow regime*. The magnitude of the R_e at which full turbulence will commence, depends on surface roughness and particle shape.

As the extra mass of turbulent water grows, the reduction in settling velocity rises sharply. Fully developed turbulence does not add to the mass that moves the particle along under gravity: it only increases the effective particle diameter. Hence, the particle's drag increases, retarding its settling velocity. Determined by the sedimentary methods the sizes of such particles are registered at smaller esds than predicted by Stokes' Law. Correspondingly, they have higher than should be cmp values.

The upper particle size limit for all sedimentary methods is calculated by using the following equation, which was derived for a R_e of 0.25 (Allen, 1995):

$$D_{uc} = \left[\frac{4.656\eta^2}{\rho_f g(\rho_s - \rho_f)} \right]^{1/3} \qquad \text{Eq. 1.5.1.1.1.2}$$

For ρ_s, the average clay density of 2,65 g/cm^3 is normally used. This is virtually the same as the densities of kaolinite and quartz, the average for all silicates and hence for most soils. At 35 °C, which is the normal operational temperature of the Sedigraph, the viscosity of water (η) is 7.165 x 10^{-4} Pa.s., and the density of water (ρ_f) is 994.0352 kg/m^3 (Table 1.4.2.1). Using these values, the upper size limit for Sedigraph analysis of the average clay is calculated at 52.9 µm.

However, the density for illite can vary between 2.6 g/cm^3 and 2.9 g/cm^3 (Deer *et al.*, 1966), and the density of Ca-montmorillonite in the presence of a dispersant is 3.00 g/cm^3 (section 1.5.8.2.2). Using these densities, the upper size limit for the Sedigraph is calculated at 50.5 µm for the maximum illite density, and 49.6 µm for Ca-montmorillonite (Eq. 1.5.1.1.1.2). Therefore, in realistic terms, 49.6 µm must be regarded as the *upper size limit* for accurate Sedigraph analysis of all soils and soft sediments of which the mineral composition is unknown.

This upper size limit for clays is very close to the largest particle size found in nature (50 µm). Therefore, analyses of unknown clay mixtures will automatically be done within the upper size limit for the Sedigraph. The other sedimentary methods are normally conducted at lower room temperatures, causing higher liquid densities and lower viscosities. Their upper limit will therefore be slightly below 49.6 µm (see Eq. 1.5.1.1.1.2).

The accuracy of an esd, when registered right on the upper size limit, can be evaluated in the following way (Allen, 1995): If the maximum allowable diameter of 49.6 µm is inserted in the equation for the Reynolds number (Eq. 1.5.1.1.1.1), its settling velocity is calculated at 3.63 x 10^{-3} m/sec.^{2}. When this, in turn, is inserted in the Stokes equation (Eq. 1.4.1.1), it gives a Stokes diameter of 48.8 µm. This means that there will be a particle size error of: 49.6 µm – 48.8 µm = 0.8 µm. This represents an error in clay particle size of 1.62% at the upper size limit of the sedimentary methods (49.6 µm).

1.5.1.1.2 Brownian diffusion and the lower size limit

Brownian diffusion is the dispersion of the small particles of a suspension brought about by the thermal motion, or thermal vibration, of the molecules of the suspension medium (van Olphen, 1977). The smaller the particle, the larger the diffusive effect.

Thermal motion causes liquid molecules to repeatedly collide from all sides with the suspended particles. Collisions along different directions continually vary in strength. Hence, small particles exhibit random vibrations, which is called Brownian motion. For the same reason, different particles have a net translation in different directions. As a result, similar to the diffusion of ions through a liquid, smaller particles are dispersed randomly throughout a suspension.

As the size of suspended particles decreases, its vertical translational displacement due to Brownian movement eventually increases enough to equal that of its downward settling displacement (Moore and Orr, 1973). Consequently, as particles decrease in size towards a limiting value, their settling velocity is increasingly retarded. This causes their cmps to be higher than those predicted by Stokes' Law. As a result, an accurate sedimentary particle size analysis cannot be obtained for particles smaller than a lower size limit.

The minimum particle size at which an accurate analysis is still possible (D_{min}), can be calculated by the following formula (Allen, 1995):

$$D_{\min} = \left(\frac{21600\ kT\eta}{\pi\ (\rho_s - \rho_f)^2 g^2 t} \right)^{\frac{1}{5}} \qquad \text{Eq. 1.5.1.1.2.1}$$

with g the gravitational acceleration, t the analysis time, k the Boltzmann constant (1.381×10^{-23} J/K), T the absolute temperature, and η the liquid viscosity. Allen (1995) stipulated that if more than 10% of a distribution falls below this size limit, then sedimentary methods should not be used to obtain its size distribution.

Using Eq. 1.5.1.1.2.1, the smallest size of clay particles to still give an acceptable accuracy (D_{min}) was calculated for the Sedigraph. To be able to use Eq. 1.5.1.1.2.1, the Sedigraph analysis time is needed. Depending on the cell scan rate, the analysis time (t) from the largest particle size (D_{max}) down to the minimum allowable size can be calculated with a regression formula (obtained by means of CurveExpert[2] from the experimental values in Table 1.5.1.1.2.1). However, to calculate t with the regression formula, the unknown minimum

[2] *CurveExpert Ver. 1.37 Curve-fitting software, D Hyams, http://home.comcast.net/~curveexpert/*

particle size needs to be known in advance – which is an impasse situation. Therefore, to be able to use Eq. 1.5.1.1.2.1, both t for any chosen scan rate, as well as D_{min}, had to be calculated simultaneously.

This was achieved as follows, by using dead reckoning in Microsoft Excel[3]: Equation 1.5.1.1.2.1 was used to calculate the minimum particle size from manually inserted analysis time ("Calculated D_{min}" and "Chosen t", respectively, Table 1.5.1.1.2.1). At the same time, the regression formula was used to calculate the analysis time from the calculated minimum particle size ("Calculated t" and "Calculated D_{min}", respectively). The chosen t was manually increased until the calculated t had the same value. This was done for three D_{max} values *viz.* 30 µm, 40 µm, and 65 µm. Thus, the Calculated D_{min} is the lower limit for the sedimentary methods.

During the calculation, the average density of clay was used for ρ_s (2650 kg/m^3: the same density as for kaolinite and quartz), and T was the normal operating temperature of the Sedigraph at 308K (35 °C). At this temperature the viscosity of water (η) is 7.165 x 10^{-4} Pa.s, and its density (ρ_l) is 994.0352 kg/m^3 (see Table 1.4.2.1).

When calculated with dead reckoning, the analysis time for Sedigraph analysis will be 1498 sec. from a D_{max} of 30 µm down to 2 µm. The minimum clay size for acceptable accuracy under these conditions is 0.56 µm (Table 1.5.1.1.2.1). The other sedimentary methods operate at room temperature, therefore for them this size limit will be at a slightly larger particle size.

From Table 1.5.1.1.2.1 it is clear that when the Sedigraph is adjusted for higher D_{max} values, the analysis time (t) decreases. At higher D_{max} values, the effect of Brownian diffusion therefore increases (Eq. 1.5.1.1.2.1). Hence, when using the Sedigraph, the minimum particle size to avert inaccuracy due to Brownian movement lies between 0.56 µm and 0.59 µm (depending on the chosen D_{max} value). Based on the calculations of the last two sections, the total particle size range for safe analysis with the Sedigraph lies between a minimum of 0.56 µm and a maximum of 49.6 µm. These size limits are applicable to kaolinite, quartz, and most soils that consist mainly of silicates.

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[3] *Excel 2000 spread sheet software for Windows, Microsoft Corporation, http://www.microsoft.com*

Table 1.5.1.1.2.1. Time at 35°C to analyse to different particle sizes using a D_{max} of 30µm, 40µm, or 65µm.

	AT Dmax = 30 µm			AT Dmax = 40 µm			AT Dmax = 65 µm		
	EQUIVALENT SPHERICAL DIAMETER (µm)	ANALYSIS TIME at 35°C		EQUIVALENT SPHERICAL DIAMETER (µm)	ANALYSIS TIME at 35°C		EQUIVALENT SPHERICAL DIAMETER (µm)	ANALYSIS TIME at 35°C	
		Experimental Values (Min.)	Calculated Values (Min.)		Experimental Values (Min.)	Calculated Values (Min.)		Experimental Values (Min.)	Calculated Values (Min.)
							65.00	0.0	0.0
				40.00	0.00	-0.02	40.00	0.20	0.24
	30.00	0.00	-0.04	30.00	0.37	0.44	30.00	0.33	0.35
	20.00	0.82	0.94	20.00	0.77	0.92	20.00	0.63	0.56
	10.00	2.72	2.85	10.00	2.23	2.08	10.00	1.20	1.16
	8.00	3.68	3.68	8.00	2.65	2.62	8.00	1.48	1.46
	6.00	5.22	4.96	6.00	3.83	3.49	6.00	1.95	1.95
	5.00	6.25	5.91	5.00	4.33	4.16	5.00	2.32	2.34
Formula to calculate Dmin	4.00	7.33	7.24	4.00	4.87	5.12	4.00	2.92	2.93
	3.00	8.53	9.23	3.00	6.27	6.63	3.00	3.88	3.90
	2.00	12.80	12.56	2.00	9.50	9.33	2.00	5.82	5.81
	Calculated Dmin	Chosen t (sec.)	Calculated t (sec.)	Calculated Dmin	Chosen t (sec.)	Calculated t (sec.)	Calculated Dmin	Chosen t (sec.)	Calculated t (sec.)
Eq. 1.4.1.1.2.1:	0.56	1497.58	1497.58	0.57	1310.30	1310.30	0.59	1111.51	1111.51
Eq. 1.4.1.1.2.2:	0.21	1944.40	1944.40	0.21	1970.54	1970.54	0.19	2867.15	2867.15

Regression formulas: Calculated analysis time from D_{max} (30 µm): $t = (39.489144 + 1.3337759 \times esd)/(1+1.0035057 \times esd + 0.018631979 \times esd^2)$

Calculated analysis time from D_{max} (40 µm): $t = ((46.317542 - 1.168351 \times esd)/(1+1.9296082 \times esd - 0.036660058 \times esd^2)) \times 60$

Calculated analysis time from D_{max} (65 µm): $t = ((212.11401 - 3.2687896 \times esd)/(1+17.660996 \times esd - 0.23202881 \times esd^2)) \times 60$

If Eq. 1.5.1.1.2.1 is reworked in terms of the γ-ratio (the mean ratio of the upwards component of Brownian movement in relation to the downward settling distance), the following formula is obtained:

$$\gamma = \frac{18}{\Delta\rho g D_{\min}^{-\frac{5}{2}}} \left(\frac{2kT\eta}{3\pi t} \right)^{\frac{1}{2}} \qquad \text{Eq. 1.5.1.1.2.2}$$

where $\Delta\rho$ is the density difference between particle and sedimentation liquid. The amount of Brownian diffusion still giving acceptable accuracy will give a γ-ratio that is equal to, or less than 0.1 (Brugger, 1976). This is when the settling distance is equal or more than 10x the distance travelled by a particle due to the upward component of Brownian diffusion.

From Eq. 1.5.1.1.2.2 it is deduced that if the γ-ratio is too large, it will give inaccurate results due to Brownian diffusion, the following can be done to reduce it to acceptable levels:

- decrease analysis temperature
- change to a liquid with lower viscosity and density (provided there is a known deflocculant for this clay/liquid combination)
- increase the field force (*viz.* by substituting gravity with centrifugal force)
- analyse to a larger minimum particle size
- enlarge the analysis time.

Due to Brownian diffusion, the smallest clay particles stay dispersed indefinitely. In other words, there is also a size limit beneath which no sedimentation takes place anymore. This will happen when the downward settling distance equals the upwards component of Brownian diffusion, *i.e.* when γ = 1. By again using dead reckoning, this particle size was calculated at 0.21 µm for all three D_{max} values (Table 1.5.1.1.2.1). Therefore, during Sedigraph analysis all clay particles of 0.21 µm and smaller will not settle at all. Since the other sedimentary methods operate at room temperature, for them this size limit will be at slightly larger particle sizes.

Summary and Conclusions for sections 1.5.1.1.1 and 1.5.1.1.2:

1) During Sedigraph analysis clay particles of 0.21 µm and smaller will permanently stay in suspension. This is so close to the lower particle size limit for the Sedigraph (0.56 µm) that care must be taken not to analyse to esds below this value.

2) Most natural clays fall within the silt size fraction below 50 µm, and will therefore not give problems at the upper limit of 49.6 µm for Sedigraph analysis. Other silicates, however, frequently have larger particle sizes than that. Therefore, before proceeding with any sedimentary method, all samples need to be separated at 50 µm, either by means of wet sieving or by sedimentary size fractionation.

3) When the Sedigraph is adjusted for lower D_{max} values, the effect of Brownian diffusion decreases. Then the minimum particle size that can be analysed with acceptable accuracy will be slightly smaller. Therefore, analyses must be conducted at the lowest possible D_{max} a clay sample allows.

4) With most analyses during this study, 2 µm was chosen as the smallest particle size. Down to 2 µm, it takes about 12 min. per analysis. However, analysing down to the lower limit of the sedimentary methods (0.56 µm) takes 42 min., which was not considered to be worth while: The lower limit is only 1.44 µm smaller than 2 µm, which would add only 4.8% to the total particle size range of the kaolinites used. This would not provide any additional information applicable to the aims of this study, but would have taken 3.5 times longer.

1.5.1.2 Magnitude of the effect of Brownian diffusion with the sedimentary methods

Brownian diffusion is very small under centrifugal force (see Equations 1.5.1.1.2.1, and 1.5.1.1.2.2). Therefore, the centrifugal particle size analysis methods can be used as standards to determine the magnitude of the error caused by Brownian diffusion during the gravitational methods. For this the results of Allen and Baudet (1977) can be employed. They compared the Sedigraph and Andersen pipette method with and a few centrifugal methods.

From their results it is clear that at the smallest particle sizes (0.2 µm – 2 µm) the Sedigraph gave large differences in cmp with the ordinary laboratory centrifuge (Table 1.5.1.2.1). It is concluded here that Brownian dispersion should have a much larger contribution to these discrepancies than hindered settling – despite the much higher solid concentration of the Sedigraph (2.0% solids by volume for the Sedigraph vs. 0.6% for the laboratory centrifuge). Proof of this is the much higher cmp values of the Andreasen pipette as compared to the centrifugal methods at smaller particle sizes, despite their *similar solid concentrations*. See for instance the substantial difference between the cmp values of the Andreasen method (0.6% solids) and that of the laboratory centrifuge of same solid concentration (0.6% solids) (Table 1.5.1.2.1). Furthermore, all the cmp differences between the Andreasen method and the laboratory centrifuge are very similar in magnitude as the

latter's differences with the Sedigraph – despite the large solid concentration of the Sedigraph. This confirms the conclusion that Brownian diffusion must have a larger effect than hindered settling in the Sedigraph.

Further confirmation is that these discrepancies between both sedimentary methods and the laboratory centrifuge are especially large at the esds nearest and below 0.56 μm, where Brownian diffusion starts to take noticeable effect. Just above the lower size limit for the sedimentary methods (0.6 μm) the Sedigraph has a 25.2% difference with the laboratory centrifuge. The difference at 0.6 μm between the Andreasen pipette and the laboratory centrifuge is nearly the same (24.4%), despite the fact that both have the same solid concentrations. These experimentally determined differences clearly illustrate the magnitude of the effect of Brownian diffusion on accuracy of the sedimentary methods at its lower size limit.

Table 1.5.1.2.1. Illustration of the magnitude of Brownian diffusion with the sedimentary particle size analysis methods

EQ. SPH. DIA. (μm)	CUMULATIVE MASS PERCENTAGE				
	LAB CENTRIF. (0.6% Solids)	SEDIGRAPH (2.0% Solids)		ANDREASEN PIPETTE (0.6% Solids)	
	Experimental	Experimental	Diff. with Lab Centrifuge	Experimental	Diff. with Lab Centrifuge
0.2	26.0	62.0	36.0	44.0	18.0
0.4	50.0	75.2	25.2	74.2	24.2
0.6	56.6	81.8	25.2	81.0	24.4
0.8	78.3	85.5	7.2	85.0	6.7
1.0	87.4	88.0	0.6	86.9	-0.5
2.0	99.1	96.0	-3.1	94.5	-4.6
3.0	-	99.5	-	98.2	-

Cmp values obtained from Allen and Baudet (1977).

1.5.2 Low X-ray absorbency of clay minerals causing high solid concentrations

In order to give an accurate analysis during X-ray sedimentometry, clay samples need to be at relatively high solid concentrations. The need for such high concentrations is due to the low X-ray absorbency of all clay minerals caused by their low density of between 2.55-2.9

g/cm^3 (average 2.65 g/cm^3) (Goldstein *et al.*, 1981). The same generally holds true for most silicates found in soils. For the Sedigraph 5000D the minimum solids content to meet this requirement for clays was determined at 3-4% by volume (section 4.2.2.1).

However, at this solid concentration, particles settle close enough to each other to have a mutual influence on each other's terminal settling velocity. This is called hindered settling (Steinour, 1944; Kynch, 1952; Richardson and Zaki, 1954). This causes an in-built inaccuracy for all X-ray sedimentometry methods. There are two types of hindered settling: low and high concentration hindered settling (Allen, 1995).

1.5.2.1.1 Low concentration hindered settling

At very low solid concentration of between 0.05% and 0.2% by volume, particles do not to influence each other's settling movement. However, when increasing the solid concentration slightly above this range, single particles move close enough to each other to increase their settling velocities above those at infinite separation (Allen, 1995).

When two spherical particles fall side-by-side, it is easier for water to flow around them rather than between them. Thus, the drag of both particles is reduced, which is the reason why their settling velocities increase (Kaye and Boardman, 1962; Kaye, 1981; Hall, 1956). This effect increasingly comes into play when particles fall closer than 10 diameters from each other.

However, when two particles are moving close enough, they may combine into a cluster (Happel and Brenner, 1965). A larger, faster moving particle can for instance pick up a smaller one as a "revolving satellite" to increase its settling velocity. Moreover, if two same-sized spherical particles move line astern: the trailing particle will accelerate in the slipstream of the leading one, until they move faster as one (Oseen, 1927).

When enough of such particle clusters combine they may form clouds, similar to density currents. The densities of such a cloud may differ from a neighbouring one. The heavier clouds will sink faster than their individual constituents would have travelled, while the neighbouring *lighter* clouds will be forced to *flow upwards* towards the top of the suspension (Kuenen, 1963; 1965a, b; 1968). Kuenen called this phenomenon "settling convection".

The combined effect of all the above phenomena will magnify as the solids content is increased from 0.2% (0.05% for line start suspensions) up to 1.0% by volume. Spherical particles with a *narrow size range*, at up to 1% concentration, can have settling rates of up to 1.6 to 2.4 times higher than when at very dilute concentrations (Jovanovic, 1965; Johne, 1965;

Koglin, 1970).

Lastly, at the top of the suspension, smaller particles are increasingly left behind due to the faster settling of larger ones. The resultant lowering in concentration higher up in the suspension increasingly causes less hindered settling for smaller particles (Davis and Hassen, 1988; Hassen and Davis, 1989). Thus, in stable suspensions with wide size ranges, a diffuse top portion characteristically develops. Davis and Hassen (1988) call this "self-induced hydrodynamic diffusion". Because of this, the accuracy of determination of the larger particles is affected more than that of smaller ones.

Due to their wide size distributions, all clay suspensions are susceptible to this effect. It is even more enhanced when dissimilar particle densities at different particle sizes add to an even wider difference in settling velocities. Such is the case of clay mixtures containing substantial portions of montmorillonite: it concentrates in the small particle sizes, and due to swelling has a much lower density than the other components.

The increase in sedimentation velocity of the affected particles leads to noticeable inaccuracy in their sedimentary particle size analysis results (Kaye, 1981). It is concluded here that suspension at concentrations between 0.05% and 1.0% will exhibit higher cmp values than should be at larger esds. This is because the particle clusters caused by hindered settling will be added to them. Accordingly, lower cmp values will be registered at the particle size fraction from which the single particle components of the clusters were extracted.

However, for powders with a wider range in particle sizes (as with clay suspensions) the increase in velocity due to hindered settling is less pronounced (Barford, 1972; Jayaweera *et al.*, 1964). Davis and Kaye (1970) observed that for particles with a wider size range virtually no clusters formed up to a 0.414% volume concentration. Therefore, to keep *low* concentration hindered settling at bay for clay suspensions, it is advisable to keep the solid concentration below 0.41% (Allen, 1995). According to the method of Gee and Bauder (1986), the Andreasen pipette analysis of clays is conducted at approximately 0.38% solids, which will exempt it from the inaccuracy caused by low concentration, hindered settling.

1.5.2.1.2 High concentration hindered settling

As particle concentrations are increased over 1% by volume, the opposite effect than with low concentration hindered selling will result: settling velocities will start to decrease again. By the time approximately 5% vol. concentration is reached, noticeably lower settling velocities than predicted by Stokes' Law will result (Kaye and Boardman, 1962). This is

called high concentration hindered settling.

Two types of high concentration hindered settling can be distinguished *viz.* that at intermediate solids contents, and that at a very high solids contents.

(a) High Solid concentration region of between 1-30%:

As solids content increases between 1% and 30%, two factors of *kinematic* type, and one of *dynamic* type, will increasingly retard settling velocity. The first kinematic factor is the upward flow of suspension-liquid displaced by the falling particles below it (Kynch, 1952). The second one is the partitioning of the gravitational drag and pressure forces between sediment and suspension-liquid (Thacker and Lavelle; 1977a, b).

Kinematic hindering, though, is not enough to account for the observed reduction in settling velocity. Thacker and Lavelle (1977a, b) also identified a dynamic hindering. It is caused both by the modification of the flow field around sedimenting particles by other nearby particles, and by turbulence likely to develop with the increased up-flow.

These three effects are increasingly enhanced at larger solid concentrations, and are collectively called *high concentration hindered settling*.

Furthermore, in suspensions with solids contents between 1% – 30% but with *wide size distributions*, as with clay suspensions, particle size segregation develops. This is visible as multiple boundaries in the top part of the suspension (Kaye and Davis, 1962; Davis, 1968/69). Each boundary represents a grouping of similar sized particles that sweeps up the smaller particles by its suspension-liquid return-flow to the layer above it. Thus, any settling of the smaller particles is prevented until the larger particles have receded. Hence, the accuracy of the results at smaller clay particle sizes will be affected.

In conclusion, the solid concentration of the Sedigraph (3-4% by volume) already falls within the high concentration hindered settling region. The question now is: will its results be affected? Careful measurements done by Martin (1941) and Anon. (1968) have shown that when all particle sizes are under 50 μm, then free fall conditions might even prevail at a 1% volume concentration. Sometimes relatively accurate measurements can even be conducted up to a volume concentration of 3%, with only marginal errors caused by high concentration hindered settling.

From the above it is concluded that at the relatively high Sedigraph solid

concentration, its results should already start to show signs of inaccuracy due to hindered settling. With this in mind, the magnitude of inaccuracy due to such a high solid concentration of the Sedigraph 5000D was also determined experimentally (section 4.2.2.3).

(b) Very high Solid concentration region of over 30%:

At high enough solid concentrations of over 30%, hindered settling results in particle interactions that leads to a further, and dramatic *reduction* in settling rates. At these high concentrations, an interlocking mechanism between particles causes them to settle *en masse*, while multiple boundaries still forms in the upper part (Davis, 1968/69).

With both types of high concentration hindered settling, the size distributions at all esds will have much higher cmps than it should have. Both will therefore cause the registering of esds smaller than their true values (Hassen and Davis, 1989). At very high solid concentrations, the resultant inaccuracies will be most pronounced.

1.5.2.1.3 Sedigraph vs. Andreasen Method

At 2-3% volume concentration, a Sedigraph analysis is already above the 0.41% margin to prevent hindered settling. However, the Andreasen method (± 0.38 – 0.6% by volume) will still be in the low concentration hindered settling region, with little effect on its accuracy. This suggests that there should be noticeable differences between their results.

To determine how much the effect of hindered settling will cause discrepancies between them, data from seven different authors who compared these two methods were assembled. The samples were divided into high, and low solid concentration groups. A summary of the differences between the Sedigraph and Andreasen results of each author are presented in Tables 1.5.2.1.3.1 (a) and (b).

The high solid concentration group consisted of data from 163 different soils samples of 6 different authors. During these analyses the solid concentrations of Sedigraph samples varied between 1.86% and 3.00% solids by volume, and for the Andreasen method between 0.42% and 1.86%. The second group of low solid concentration results consist of three kaolinite samples. Here the solid concentration varied between 0.42% to 0.94% by volume for both the Sedigraph and the Andreasen method.

Table 1.5.2.1.3.1 (a). Difference between Sedigraph and Andreasen pipette results, with the Sedigraph analysis conducted at high solid concentration

EQ. SPH. DIA. (µm)	SEDIGRAPH CMP minus ANDREASEN PIPETTE CMP HIGH SOLIDS CONCENTRATION						Average Difference High Solids
	Allen & Baudet (1977)	Welch et al. (1979)	Berezin & Voronin (1981)	Weaver & Grobler (1981)	Coates and Hulse (1985)	Buchan *et.al.* (1993)	
Sedigraph	(Kaol. 2.0% Solids*)	(2.2% Solids)	(0.7-1.16% Solids)	(1.5% Solids)	(?% Solids)	(±1.86% Solids)	
Andreasen	(Kaol. 0.6% Solids#)	(0.42% Solids)	(?% Solids)	(1.5% Solids)	(?% Solids)	(±1.86% Solids)	
0.2	18.0						18.0
0.4	1.0						1.0
0.6	0.8			5.4			3.1
0.8	0.5			5.4			2.9
1	1.1		12.5	7.0			6.9
2	1.5	3.1	13.3	8.4	1.3	6.6	5.7
3	1.3	4.1	13.8	6.8	0.8	7.1	5.7
4		5.1	14.0	5.1	0.5	7.3	6.4
5		5.9	13.8	3.8	0.2	7.4	6.2
8		8.0	11.2	1.4	-0.2	7.4	5.6
10		8.9	7.9	0.7	-0.4	7.3	4.9
16		9.8		0.6	-0.1	7.0	4.3
22		10.8			1.2	6.7	6.2
30		18.4			5.0		11.7
44					7.0		7.0
50		3.9	4.1				4.0

Al solids concentration values are for soils, except where indicated differently

Table 1.5.2.1.3.1 (b). Difference between Sedigraph and Andreasen pipette results, with the Sedigraph analysis conducted at a low solid concentration

EQ. SPH. DIA. (μm)	SEDIGRAPH CMP minus ANDREASEN PIPETTE CMP LOW SOLIDS CONCENTRATION		
	Welch et al. (1979)		Watts et al. (2000)
Sedigraph	(0.85% Solids)	(0.42% Solids)	(Kaol. 0.94% Solids)
Andreasen	(0.42% Solids)	(0.42% Solids)	(Kaol. 0.94% Solids)
0.2			
0.4			
0.6			1.2
0.8			2.9
1			3.8
2	-0.6	-2.3	4.3
3	-0.3	-2.2	3.7
4	0.0	-2.1	3.2
5	0.2	-1.9	2.8
8	0.8	-1.5	2.1
10	1.1	-1.3	1.8
16	2.1	-0.4	1.3
22	3.8	0.6	0.8
30	6.1	1.9	0.3
44			-0.5
50			-0.8

From both Tables 1.5.2.1.3.1 (a) and (b) it is evident that when Sedigraph analyses are conducted at the same low solid concentration as the Andreasen pipette, then the results show a reasonable comparison. But, at high Sedigraph solid concentrations the differences in cmp values are very larger.

Since the Andreasen method has been used for many decades in many disciplines, it is still viewed by many as the standard method for particle size analysis. However, with such good comparison between the two methods at the same low solid concentration the question is: which method to use as standard procedure? When comparing Sedigraph 5000D and pipette results with that of optical studies, Weaver and Grobler (1981) found that the Sedigraph was the more accurate method. It is suggested here that the likely reason for this is that the suspension is repeatedly disturbed when the pipette is lowered and withdrawn to remove aliquots for drying and weighing. Furthermore, larger particles than intended will be sucked in from below the tip of the pipette, which should also affect accuracy. Additionally, any variation in speed of withdrawal and lowering, and differences in suction should furthermore affect

reproducibility. When, its much shorter analysis time and greater ease of operation is also taken into account, then the Sedigraph is the obvious choice as standard method for gravitational sedimentary particle size analysis (Lara and Matthes, 1986; Watts *et al.*, 2000).

Should, however, the standard method be changed to the Sedigraph, a way of comparing its results with the vast amounts of Andreasen pipette results in literature is needed. Welch *et al.* (1979) and Buchan *et al.* (1993) supply regressions formulas, with good correlation coefficients, to convert Sedigraph cmp values below various particle sizes to Andreasen pipette values.

1.5.3 The possible effect of clay particle rotation

Ideally, clay particles are platy monoclinic or triclinic minerals, with pseudo-hexagonal shapes (Fig. 1.5.3.1). Electron micrographs, though, reveals that most clay platelets have an irregular shape when viewed from above (Beutelspacher and van der Marel, 1968; Sudo *et al.*, 1981). Some clay types, like halloysite, have internal stresses due to irregular staking of layers. This, along with the presence of inter-layer water, often causes halloysite platelets to roll into tubular shapes (Bates *et al.*, 1950).

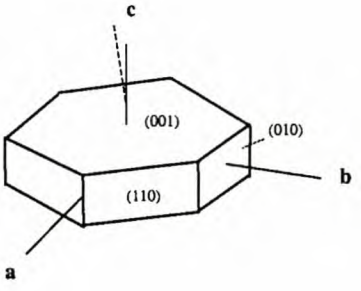


Fig. 1.5.3.1. Typical pseudo-hexagonal shape of a well-crystallised clay particle, along with its crystallographic axes (after Deer *et al.*, 1966).

The results of hindered settling are covered extensively in the literature; yet, no mention is made of the effect of particle rotation on settling velocity. Inter-particle collisions should cause clay platelets to spin round an axis parallel to its basal plain. The following is postulated to throw light on its possible effect on the accuracy of the sedimentary methods:

The smaller a clay particle becomes, the more it will be inclined to rotate due to increasing collisions from larger particles. With decrease in size, collisions by vibrating fluid molecules also enhance clay particle rotation (van Olphen, 1977). As rotation of irregular particles increases, its terminal settling velocity is reduced (Allen, 1995).

In contrast, due to their higher inertia, larger particles will less be inclined to rotate when colliding with smaller ones; they will also less be put into rotation by particles larger than themselves. Consequently, the larger a clay particle, the less its terminal settling velocity will be decreased by rotation.

As clay particles therefore become smaller, increased particle rotation should cause sedimentary methods to register lower esd values than it should have. Accordingly, their cmp values will be registered higher than should be. However, for large clay particles, the opposite should be true.

Hence, with all sedimentary methods, the smaller amount of rotation of *larger* clay particles should ensure more accurate esd and cmp values for them, than will be the case with smaller ones.

1.5.4 True clay platelet dimensions vs. the equivalent spherical diameter

It is evident that the true dimensions of clay platelets and rods (width and thickness) differ significantly from those of the diameter of a perfect *sphere* (*i.e.* the equivalent spherical diameter). Neither the actual basal diameter, nor the thickness of the clay platelet, will be anywhere close to its esd. The sedimentary methods should therefore not give any indication of the actual physical dimensions of clay particles.

The reason presented here for these discrepancies is that there should be a large difference in drag between all the different fall orientations of a clay platelet and that of a sphere. A plate-like particle should fall in four different orientations, each with unlike settling velocity. The largest velocity will be reached when a clay platelet falls edgewise, with its smallest surface orientated downward. Slower velocities will be reached when a clay platelet falls with its flat surface in a perfect horizontal orientation. An even lower velocity will be reached when it rotates. The slowest fall-velocity will probably be when it falls like a leaf: floating from side to side, with its flat surface at a slight angle. Reduction in settling velocity will lead to smaller esd values than should be. None of the downwardly presented dimensions of each fall orientation will be the same as the diameter of the sphere settling alongside it.

The question now is: how large is the discrepancy between the experimentally determined esd of a clay platelet and its actual basal diameter and thickness? Jennings (1993) and Lu *et al.* (2000) derived equations to calculate the true dimensions of clay particles from their experimentally determined esds. Jennings calculated for the average clay platelet with an esd of 2 μm a true basal diameter of 4.70 μm, and a thickness 0.47 μm; while with their formula,

Lu *et al.* (2000) calculated a true basal diameter of 5.2 µm, and a thickness of 0.52 µm. With both authors the clay platelet aspect ratio[4] was $h/D = {}^{1}/_{10} = 0.1$. Experiments of both confirmed their calculations.

The above implies that the true basal diameter of a clay platelet will be between 240% and 260% the size of its esd. The thickness will differ with between 24% and 26% the size of the esd. Well-crystallized kaolinite can even have aspect ratios of up to 100/1, which will give it a basal diameter of up to 800% and a thickness of about 8% of its measured esds (Lu *et al.*, 2000). For halloysite, Lu *et al.* (2000) calculated its cylinder length to be 400% longer than its esd. The above clearly proves that the diameters of clay particles determined by sedimentary methods do not even come close to their actual dimensions.

There is another method to calculate the true dimensions of clay platelets and rods from experimental particle size analysis results (Slepetys and Cleland, 1993; Jennings, 1993). These authors developed formulas that use the experimental diameters obtained by a combination of any two of the following types of particle size analysis methods: sedimentation, light scattering, optical birefringence, Mie-theory angular light scattering, the Coulter principle, photon correlation scattering, and rotary motion.

The question now is: since the esd differs so much from the true dimensions of irregular particles, of what use is the sedimentary methods to the field of sedimentology? The answer lies in the fact that the hydrodynamic equations describing the settling behaviour of any particle during different flow situations in a liquid make use of particle diameter and settling velocity. The sedimentary particle size analysis is the only method that gives a diameter directly related to terminal settling velocity. Hence, the esd is the only experimentally determined diameter that can be used with hydrodynamic calculations.

1.5.5 Larger tendency of clay particles to flocculate

Flocculation is the coagulation in water of single particles into loosely bound particle assemblies due to attractional electrostatic forces (van Olphen, 1977). However, to accurately determine the particle size of a powder, its particles must be separate, otherwise flock sizes are registered in reality.

To ensure accurate particle size analysis results it is important to first understand the causes and mechanism of clay flocculation. In this way, a correct procedure for deflocculation (peptization or stabilization) clays can be derived by which to secure the accurate diameters of

[4] *D* is *the largest diameter of the basal surface for a clay disk, and h its thickness.*

single clay particles.

1.5.5.1 Causes of flocculation

Clay platelets carry a net negative (–) charge on their large *basal surfaces*. However, along their smaller *edge surfaces*, the sign of the net surface charge depends on pH. The edge-charge has a net positive (+) value at a more acidic pH, no charge at just above a neutral pH, and a net (–) charge at a higher, alkaline pH (Schofield and Samson, 1953). It is especially this unique pH dependant dual nature of the edge-charge of clays that is of significance in flocculation and peptization of clays.

A second important factor determining the stability of suspensions is the reduction of the thickness of the clay particle double layers by the increase in salt concentration (van Olphen, 1977).

To understand the reasons and mechanisms of flocculation/deflocculation the origin of the surface charge on both the basal and edge surfaces needs to be explained first. Thereafter the origin and dual nature of the clay particle double layer, and its effect on flocculation/ deflocculation according to the pH and dissolved salts concentration, will be given in short. After that, the use of chemical agents (deflocculants) to obtain complete deflocculation by will be described.

Lastly, the contribution of the platy shape of clay particles to its larger tendency to flocculation will be explained.

1.5.5.1.1 The origin of clay surface charge

Due to their relatively high surface charges, clays tend to flocculate more easily than other minerals. This is proven by their exceptionally high ion exchange capacities and surface charge densities (Grim, 1962; Anon, 1951).

(a) Surface charge of clay minerals along its basal surfaces:

The larger flat basal surfaces of all clays have a net (–) surface charge. Apart from kaolinite, it results from the isomorphous substitution of Si^{4+} by Al^{3+} in the tetrahedral silica layers (Schofield and Samson, 1953). In some clay minerals (notably the *swell-clays* and *vermiculite*), there is also substitution in the octahedral alumina layers. Here Al^{3+} is replaced by other similarly sized ions of lower valence (Mg^{2+}, Fe^{2+}; and less commonly: Cr^{2+}, Zn^{2+}, and Li^{+}). Consequently, swell-clays and vermiculite exhibit a net (–) surface charge of between 0.2 – 0.9 per unit cell on their basal surfaces (Flegmann *et al.*, 1969; Rand and Melton, 1977;

Williams and Williams, 1982; Velde, 1992). With montmorillonite and vermiculite, isomorphous substitution causes up to 80% of (–) basal surface charges (Grim, 1962).

With *chlorite,* and the *palygorskite group* of clays, lattice substitution causes a smaller amount of surface charge, but it is still the major contribution to a net (–) surface charge on the basal surfaces (Grim, 1962). Due to isomorphous substitution of Si^{4+} by Al^{3+} in every fourth tetraheder, the *Illite* has the largest (–) surface charge of between 0.9 – 1.0 per unit cell (Velde, 1992).

Kaolinite also has a net negative charge on its basal surfaces (Follet, 1965; Weiss and Russow, 1963). However, here isomorphous substitution has no contribution at all. The (–) basal surface charge of kaolinites in suspension increases according to its electrolyte concentration, and is probably caused by a strongly adsorbed alumina-silicate gel (Ferris and Jepson, 1975).

The basal surfaces of all clays have additional (–) surface charges caused by broken bonds on its silica and alumina units. Such broken bonds are produced by the loss (or non-addition) of exposed Si^{4+} or Al^{3+} from incomplete tetraheders or octaheders on the surface (Grim, 1962).

(b) Surface charge of clay minerals along its thin plate edges:

Along the plate edges, the primary surface charge holds a net (+) charge; it is also caused by broken bonds (Grim, 1962). Primary (+) edge-charges are formed at the ends of the silica and alumina sheets when one or more oxygens or hydroxyls are removed from central tetrahedral Si^{4+} or Al^{3+} octahedral cations – or are not added in the first place. On the *basal surfaces* of all clays (+) charges are also produced in this manner, but are of much smaller extent than the (–) charges; thus a net (–) charge on basal surfaces dominates.

Some (–) surface charges are also found along the thin plate edges of all clays due to the already mentioned removal of exposed Si^{4+} or Al^{3+} cations (Johnson and Norton, 1941; Thiessen, 1942, 1947; van Olphen, 1950 a, 1951). But, for all clay types this (–) edge-charges are totally overshadowed by (+) edge-charges (van Olphen, 1977).

1.5.5.1.2 The theory of stability of clay minerals and the mechanism of flocculation

The theory for flocculation and dispersion of particles was jointly developed by Derjaguin and Landau (1941), Verwey and Overbeek (1948) – called in short the DLVO theory. This theory proposes that particles in suspension, which move close enough to each other, stick together due to attractional van der Waals forces, causing them to flocculate.

The van der Waals attraction is produced by charge fluctuations of all the atoms in a crystal structure caused by their thermal vibrations. This continually induces dipoles between mutually interacting atoms, with electronic attraction as a consequence. Van der Waals attraction is the compilation of all attractional forces between all atoms of adjacent particles (Hamaker, 1937). Van der Waals attraction therefore becomes larger with increase in particle size.

Van der Waals forces are in turn counterbalanced by a repulsional electrostatic force, which is induced by particle surface charge of similar sign. In water, even at very low dissolved salt concentrations, ions in solution will be attracted by the particle surface charges of opposite sign, thus neutralising it (Gouy, 1910a, b; 1917; Chapman, 1913). They are called counter ions, and are more concentrated closer to the basal surfaces, becoming more diffuse deeper into the surrounding liquid (Fig. 1.5.5.1.2.1). The charges on the clay surface along with its layer of counter ions are collectively called the diffuse double layer.

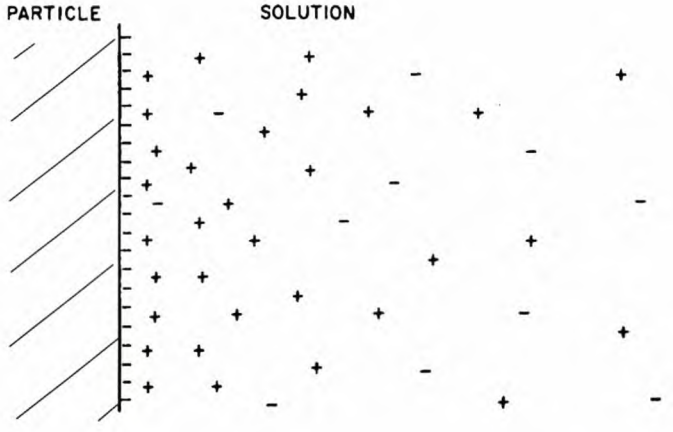


Fig. 1.5.5.1.2.1. The diffuse double-layer model according to Gouy (1910a, b) (sketch after van Olphen, 1977).

When adjacent particles move closer to each other, their counter ion layers start to overlap. When the counter ions are of the same sign, overlapping causes an increase in free energy, leading to an exponential increase in repulsion as they move closer together. At low salt concentrations the respective diffuse double layers are wide enough that their repulsion keep the particles far enough apart, to prevent van der Waals attraction to grow large enough to cause agglomeration. This leads to a deflocculated particle suspension, which is also called a stable suspension.

However, when the counter ion layers are of opposite sign, and adjacent particles move closer together, attraction increases between double layers. As a result, inter-particle distance is

further reduced, van der Waals forces increasingly supplement the attractional energy, and quick flocculation results. Such a suspension is called unstable.

A clay platelet uniquely has two different types of double layers:

- the double layer on its large basal surface that has a permanent (+) counter ion layer,
- and a double layer on the narrow edge that can *vary in sign*.

The two types of double layers are formed in the following ways:

Due to permanent (−) surface charges of the *flat basal surfaces*, its diffuse double layer is of the constant charge type, and its counter ions are *cations* (Fig. 1.5.5.1.2.1). The double layer of the basal surface is called a (−) double layer after the sign of its surface charge. Besides cations, the diffuse double layer of the *basal surfaces* also contains a smaller amount of *anions*, called co-ions, decreasing in concentration towards the negatively charged surface.

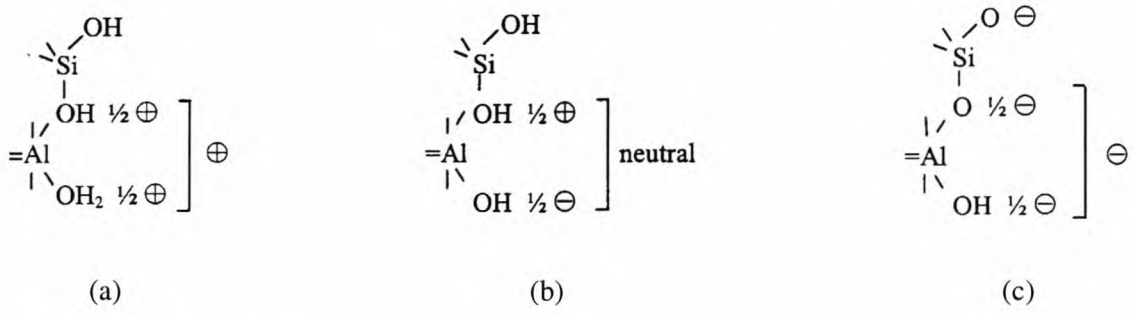
The second type of diffuse double layer along the clay particle *edge surfaces* has a sign that can either be positive, neutral, or negative, depending on the suspension pH and salt content (Schofield and Samson, 1954; van Olphen, 1964).

Along clay *particle edges* the (+) surface charge on the *alumina* layer is caused by adsorption of ions directly onto the surface charges caused by broken bonds. When surface charge has this origin then the inner coating of its double layer is produced by the adsorption of the anions of a dissolved electrolyte, called the peptizing ions. It is the latter that determines the actual surface charge. The other ions of the electrolyte supply the outer layer of counter ions of opposite sign. Such surface charge varies in strength, depending on the concentration of the peptizing ions. To be stable, such a suspension must contain a minimum amount of salt, called a peptizing electrolyte (usually less than 1 m.eq/l), which supply both the peptizing and counter-ions (van Olphen, 1977).

In distilled water, a *silica particle* always has a negative double layer at any pH. However, in clay suspensions there is a consistent presence of Al^{3+} resulting from the slight dissolution of clays always occurring in water. In the presence of dissolved Al^{3+}, the surface charge on the *edges* of the *clay silica layer* becomes (+) due to Al^{3+} adsorption (van Olphen, 1951). The surface charge alongside the *tetrahedral silica layers* is independent of pH, and will therefore always have a (+) double layer.

On the *alumina layers* along the clay edges, however, the edge-charge varies in sign according to pH. It is always larger in magnitude than that of the silica layer, and therefore has the overriding influence on the sign of the double layer on clay edges. In distilled water, at a

moderately acidic pH, the surface charge has a (+) sign. It is produced when oxygens and hydroxyl groups, which are attached to Si and Al atoms along kaolinite plate edges, become protonated. (Fig. 1.5.5.1.2.2 (a) – Schofield and Samson, 1953; van Olphen, 1964):



(a) (b) (c)

Fig. 1.5.5.1.2.2. Spatial arrangement of clay edge-charge under conditions of: (a) mildly acidic, (b) slightly alkaline (c) strongly alkaline (after Schofield and Samson, 1953).

At an acidic pH, all other clay types exhibit a (+) double layer along the edges (van Olphen, 1950 a, 1951).

When, however, the pH is increased to just above the neutral value, there will be equal amounts of (+) protonated, and (–) de-protonated hydroxyl groups attached to surface Al and Si atoms on the edges (Fig. 1.5.5.1.2.2 (b) – Schofield and Samson, 1953; van Olphen, 1964). The edge surface charge then is neutral, and the clay *edge* is said to be at its point of zero charge (p.z.c.).

When the pH in distilled water is increased to above 7, then dissolved OH^- ions remove and replace the protons adsorbed on the exposed oxygens attached to Al^{3+} ions of the crystal lattice. As the pH is increased even further, deprotonation continues, and exposed silanol groups also dissociate. Hence, the edge double layer becomes (–) (Fig. 1.5.5.1.2.2 (c) – Schofield and Samson, 1953; van Olphen, 1964):

The same happens on the silica layer along positions where Al^{3+} had substituted the tetrahedral Si^{4+}. This further enlarges the (–) character of the clay edges (van Olphen, 1977). In addition, excess OH^- anions in solution adsorb onto the small amount of positive charges also present on the basal surfaces, and neutralise them. This increases the predominately negative charge on the basal surfaces, giving it an even larger total negative value.

The change in sign of the edge double layer with change in pH, controls the unique flocculation/deflocculation behaviour of clays (van Olphen, 1950a, b). During clay flocculation three types of particle associations occurs, *viz.*. edge-to-edge, edge-to-face, and face-to-face

(van Olphen, 1961a) (Fig. 1.5.5.1.2.3).

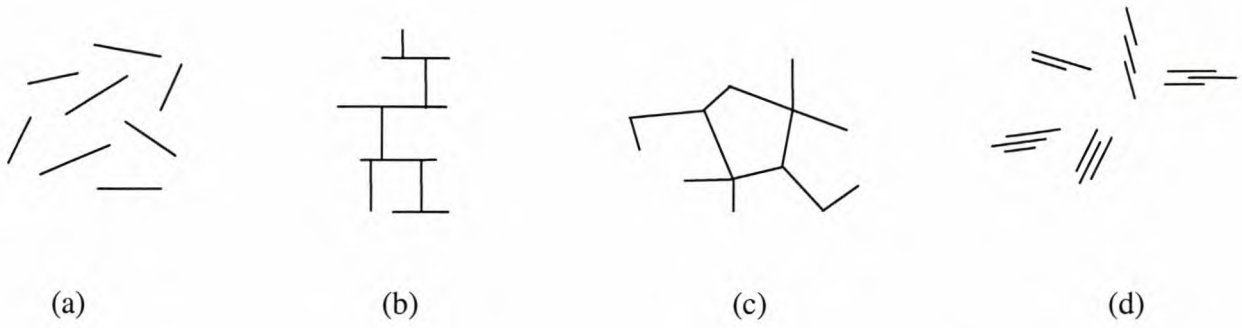


Fig. 1.5.5.1.2.3. A few modes of particle associations in a clay suspension: (a) dispersed and deflocculated (b) edge-to-face associations (c) edge-to-edge associations (d) face-to-face associations (After van Olphen, 1977).

Since pH determines the sign of the edge-charge, it will play the decisive role in which of the above particle associations will form. At low pH, the counter-ion layers of the edges and faces have opposite signs, and are therefore attractive. Hence, colliding particles immediately flocculate with edge-to-face associations.

At a pH right on their p.z.c. (points of zero charge) the neutral edges can still move close enough to negatively charged basal surfaces, as well as to other neutral edges. Hence, both edge-to-face and edge-to-edge flocculation takes place (Schofield and Samson, 1953; van Olphen, 1964). Such clay suspension is flocculated, and said to be unstable.

When the pH is increased further to more alkaline conditions, the edges have a (–) double layer ((+) counter ions), which is the same as that of the flat basal surfaces. This leads to double layer repulsion between all faces. Hence, when particles collide, they cannot move close enough for van der Waals forces to take over. Flocculation is prevented, and the suspension is deflocculated and stable.

The pH value at the p.z.c. of the edges of clay minerals is therefore of great importance during size analyses of clays. To secure accurate analysis results it should be conducted at pH values well above the p.z.c. of the edges, which is higher than a pH of slightly over 7 (sections 1.5.5.2 and 4.1.2.2).

As mentioned before, due to slight dissolution in *distilled water* clay suspensions always have enough dissolved ions to still form oppositely charged diffuse double layers. In theory, this should lead to flocculation. Surprisingly, though, a clay suspension in distilled water remains stable for quite some time (van Olphen, 1977). The same is true at very low NaCl

concentrations of ≤ 0.01M (Oss *et al.*, 1990). This stability at low electrolyte concentrations is caused is by spill-over of negative charge from the large basal surfaces onto the thin plate edges (Secor and Radke, 1984: Chang and Sposito, 1996). Due to (−) charge spill-over the edges exhibit a net negative electrostatic field, despite its net positive surface charge. This once again results in a repulsive electrostatic force between all surfaces, giving rise to the stable suspension in distilled water.

But, despite this, in distilled water a few inter-particle collisions between edges and faces are energetic enough for the repulsive forces to be overcome. With time, this leads to a slow flocculation process in distilled water, which is irreversible when such a suspension is left undisturbed (van Olphen, 1977). To ensure accurate particle size analysis such aggregates must be broken down by grinding in a mortar and pestle, or by ultrasonic treatment (Sato, 1993).

A second cause of flocculation is the *increase in salt concentration as well as the valence of the counter ions*. This causes the double layers to "compress" to become "thinner" (van Olphen, 1951). At any given distance from the particle, the repulsive potential decreases proportional to the amount of salt added (Fig. 1.5.5.1.2.4).

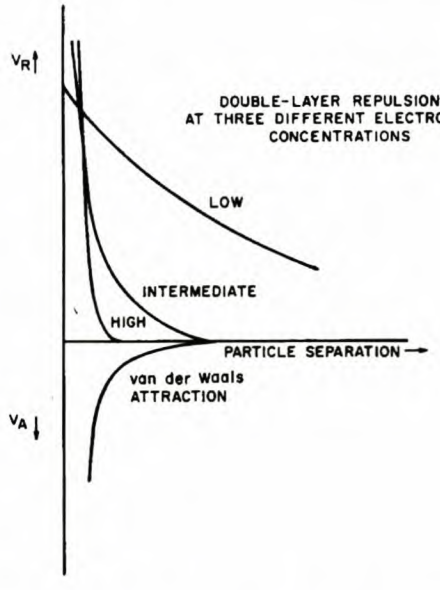


Fig. 1.5.5.1.2.4. Repulsive energy (V_R) by counter ions, and attractional van der Waals energy (V_A) as a function of particle separation at three different salt concentrations (After van Olphen, 1977).

It can be seen in Fig. 1.5.5.1.2.4 that at *low salt content*, the repulsive potential of the diffuse double layer is always appreciably higher than the van der Waals attractional potential at most inter-particle separations. Since repulsion dominates, the energy of most particle collisions is too small to move particles close enough for attractional van der Waals forces to

take over and cause flocculation. When NaCl is added, at a concentration as low as 0.005M, then additionally the (+) edge-charge is decreased by Cl^- adsorption, which also aids deflocculation. (Schofield and Samson, 1954). Flocculation occurs very slowly, and only becomes noticeable over weeks or months.

However, at *intermediate salt concentration*, the attractional and repulsive potentials are always more or less equal at larger particle separations; at closer distances, the attractional potential quickly becomes the larger of the two. Therefore, most collision energies are adequate to overcome repulsion; so, van der Waals forces take over, and cause slow flocculation.

At high salt concentration, at most distances, apart from very close up, the attractional potential is always the larger of the two. Therefore, at high salt concentrations, immediately when two particles move into the range of their van der Waals forces, rapid flocculation takes place.

The order of the amount of collision energy required for the three types of inter-particle associations to form is: edge-to-face < edge-to-edge < face-to-face. Hence, edge-to-face associations generally tend to dominate, followed by the other types in that order. Face-to-face associations only form when the double layer is compressed enough by salt for van der Waals forces to take over.

Increasing the salt concentration has the opposite effect on the stability than increasing the pH: the former causes flocculation, and the latter deflocculates the suspension. The minimum salt concentration at which a suspension starts to flocculate, at a given pH, within a given time period, is called its critical coagulation concentration (c.c.c.) (van Olphen, 1977).

Since pH determines the sign of the edge, it also determines at what salt concentration clay will flocculate – hence the magnitude of the c.c.c. In alkaline conditions, when enough salt is present in a deflocculated suspension, the negative edge-charge of all clay types can be removed by the excess cations through dissolution. This again leads to excess (+) charge at the clay edge surface, inducing flocculation (Schofield and Samson, 1954; Dickman and Bray, 1941; McAuliffe *et al.*, 1947). Hence, when more salt is added to clay suspensions, the p.z.c. shifts to higher pH values; or viewed differently, the c.c.c. increase to higher salt concentrations when the pH is increased.

In addition to decreasing the pH and adding salt, a third way that rapidly flocculates a *stable* clay suspension in distilled water is by increasing its temperature (Jackson, 1968). Although it is a well know phenomenon, an explanation for it is lacking in literature. It is concluded here that with heating a suspension the energy of particle-collisions first of all

increases due to increased Brownian movement. Secondly, like adding an electrolyte, heating also compresses the double layer. Hence, heating in distilled water also enables edges and faces to move close enough for van der Waals force to take over, and cause flocculation.

The thickness of the double layer also depends on the dielectric constant of the suspension liquid. As the dielectric constant decreases, the double layer becomes thinner, and flocculation is thus enhanced. Therefore adding polar organic solvents of lower dielectric constant than water (i.e. ethanol, methanol, acetone), will increase flocculation. Their flocculating power increases in the order ethanol, methanol, and acetone as their dielectric constants decrease in that order.

An increase in the suspension concentration will also lead to enhanced flocculation (Kaye and Davis, 1962). For this, the following explanation is offered: with an increase in concentration, particles will be closer to each other, which will cause more particle collisions per unit time. Along with the accompanying increase in hindered settling at higher solid concentrations, this will cause less accurate results.

At a high enough *solid concentration* and with enough salt present, the clay suspension gels into one voluminous flock that has various degrees of rigidity (Hauser and Reed, 1937; van Olphen, 1959; O'Gorman and Kitchener, 1973). At complete gelation edge-to-edge associations dominates with all clay minerals, but edge-to-face "card-house" structures may also be formed (Pierre, 1996; van Olphen, 1977). Under such condition no settling of any particles, flocks or aggregates can take place, and therefore all sedimentary methods become impractical.

Conclusions:

The following steps can be taken to create favourable conditions during all particle size analysis methods of clays in distilled water:

- desalination,
- increase the pH (at least higher than pH 7: the p.z.c. value of the clay edges in distilled water),
- lower the temperature,
- analyse at low solid concentration.

These steps, however, are still not enough to not create a completely stable clay suspension. In order to perform accurate particle size analysis, a chemical deflocculant must

also be added.

1.5.5.2 Conditions and methods for chemical dispersion

In order to bring about durable deflocculation of clays during particle size analysis, negatively charged organic polymer ions, so called deflocculants or peptising agents, are employed. During this study, four deflocculants were used to stabilise clay suspensions *viz.* Calgon (sodium hexametaphosphate), Dispex N40 (sodium polyacrylate), TSP (tetra sodium phosphate) (Fig. 1.5.5.2.1), and Floccotan Sudguard 3195 (a co-polymer between acrylic acid and 2-acrylomido-2-methylpropane sulfonic acid).

All of these deflocculants are sodium polymeric salts that dissociate in water into Na^+ cations, and poly-anions. The (–) polymer ions chemisorp[5] on the clay edge surfaces at exposed octahedral Al^{3+} cations, or onto Mg^{2+} or Fe^{2+} cations that substituted Al^{3+} in the octahedral sites. Some also adsorb onto the few (+) surface charges on the basal surfaces (Joyce and Worrel, 1970; Nabzar *et al.*, 1988).

Each poly-anion chain has more free (–) charges along its length than the available (+) charges on the edge and basal surfaces. Hence, only some of the poly anion (–) charges attach onto the surfaces. The rest of the (–) charges along the poly-anion chain orientate themselves outwards, away from the clay surfaces due to the repulsion from (–) surface charges. Outward rotation of (–) poly anion charges is assisted by electrostatic attraction from surrounding water dipoles and Na^+ counter ions (Fig. 1.5.5.2.1). Hence, all (+) surface charges are reversed to (–) surface charge, and a single (–) double layer is established on all surfaces (van Olphen, 1950b; Mackor, 1951; Bidwell *et al.*, 1969, 1970; Joyce and Worrel, 1970; Diz and Rand, 1990). Thus, the unique ability of clay platelets to form card-house structures is terminated due to all-round repulsion, and the suspension is completely deflocculated.

At low, or no salt content, the adsorbed polymer chains may form loops and tails extending into the surrounding solvent, that further aid dispersion. Resistance of the loops against compression, along with mutual steric interactions, helps to prevent close association with adjacent particles surfaces (Nabzar *et al.*, 1988). But at high salt content, the whole of the polymer chains orientate parallel to the clay surface (Diz and Rand, 1990). Hence, to ensure accurate results, a deflocculated clay suspension needs to be desalinated prior to particle size analysis (section 4.1.1).

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[5] *Ions and molecules chemisorp onto solid surfaces by means of true chemical bonds.*

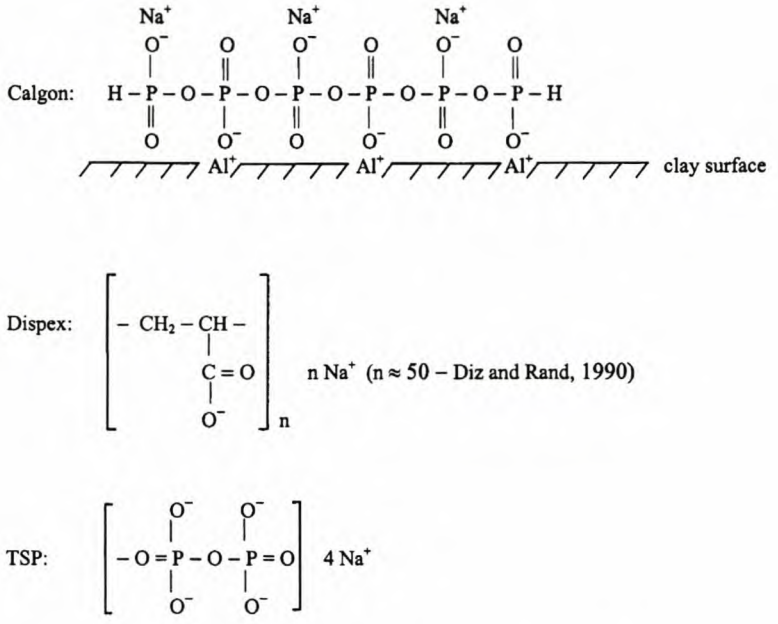

Fig. 1.5.5.2.1. The structures of three of the deflocculants used in this study (Rohmann, 1974). The Calgon structure is used to illustrate the possible chemisorption of deflocculant poly-anions on clay surfaces (after van Olphen, 1977).

Deflocculant anions adsorbs on (+) surface charges situated *both on edges, and on basal surfaces* (Diz and Rand, 1990; Miano and Rabaioli, 1994). Hence, the net (–) surface charge thus formed on the basal surfaces is larger than it was before the deflocculant was added. Therefore, in the presence of deflocculants, the diffuse double layer of basal surfaces is wider than without (Vincent *et al.*, 1971). This should lead to increased repulsion during inter-particle collisions. Hence, contrary to the case of a very dilute salt solution in distilled water, adding a small amount of deflocculant, creates a suspension that remains stable for long periods of time, even when heated (section 4.2.3.2).

A word of caution, though, is that when the deflocculant concentration is stepwise increased past a maximum value, then any clay suspension will flocculate once again (van Olphen, 1977). This may even happen at relatively low deflocculant concentrations. It is therefore advisable to always first determine the minimum amount of deflocculant to obtain full stability with any new clay sample. Thereafter, to safely disperse a clay, add just a little bit more than that (section 4.1.2.1).

However, using a Na-polymeric salt to effect deflocculation is counter-intuitive: adding an electrolyte usually causes flocculation. There are two reasons why the latter is not the case when Na-polymeric salts are added as peptizers. The first one is that the activity of its Na^+ ions is greatly reduced by the large amount of free (–) polymer anions simultaneously in solution.

This enhances the salt tolerance of the system, decreasing the flocculating power of the Na^+ in solution (van Olphen, 1950b).

Furthermore, when a deflocculant is added, it complexes the Ca^{2+} in solution, which will further enhance clay suspension stability (Gosselin and Coghlan, 1953; Zagorovskii, 1971). When Ca^{2+} is present in the clay counter ion layer, it tends to flocculate much more readily (Oakley, 1927a). The latter author was first to illustrate that Ca^{2+} had a 10x larger flocculation power than Na^+. The reasons why divalent Ca^{2+} causes increased flocculation are firstly that with the increase in cation charge, aluminium is increasingly removed from the octahedral clay layers. The dissolved Al^{3+} forms aqueous aluminium complexes, that coagulate clay particles (Swartz-Allen and Matijević, 1975). In addition, the Ca^{2+} counter ions in the double layer will neutralise (–) surface charges on the basal layers more efficiently. But, as opposed to monovalent Na^+, half the amount of divalent Ca^{2+} counter ions will be needed to accomplish this. Hence, Ca^{2+} counter ions cause thinner double layers than Na^+, and therefore cause increased flocculation. Hence, the exchange of Ca^{2+} by the Na^+ cations dramatically increases clay stability (Oakley, 1927a).

However, strong complexation by deflocculant polyanions removes almost all the alkali metal cations Ca^{2+}, Mg^{2+}, Zn^{2+}, Ba^{2+}, Cd^{2+}, from suspension (Steiner, 1935; Ha and Kim, 1969). This is especially the case with Calgon (van Olphen, 1950b). The latter forms $Ca_3(PO_3)_6$ complexes that are so strong (pKc of 1.86) that it prevent Ca^{2+} to take part in any chemical reactions or ion exchange.. In addition, monovalent Na^+, supplied by the deflocculants, takes the place of divalent Ca^{2+} as counter ions in the double layer, thereby widening it and thus decreasing flocculation.

At low pH values, where a clay suspension would normally have flocculated due to edge-to-face associations, adding deflocculants will disperse it (Michaels, 1958). However, clay dispersion by means of a deflocculant is most effective at high pH values (see the experimental results of section 4.1.2.2). Dispersion with deflocculants is therefore enhanced by increasing the pH through $CO_3^=$ hydrolysis by adding small amounts of Na_2CO_3 (section 4.1.2.2).

The addition of Na_2CO_3 first of all increases the Na^+ concentration, which aids the widening of the double layer by exchanging with Ca^{2+}. Secondly, the OH^- ions, supplied by $CO_3^=$ hydrolysis, remove H^+ from (–) surface charges, liberating even more adsorption sites for Na^+ (van Olphen, 1977). Thirdly – as seen in the previous section – at high pH, the additional OH^- reverses the (+) edge-charge on the aluminium layers. This should augment the charge-reversal of the polyanions, aiding deflocculation even further.

Lastly, during energetic stirring, shaking, or ultrasonic treatment of a suspension, the addition of deflocculants assists the break-up of clay *agglomerates* (section 4.1.3.2.1).

During sedimentation particle size analysis *in air* (called air classification), treatment with hydrophobic surfactants can be used to successfully deflocculate all silicates. Since moisture tend to adsorb on all particles surfaces, small particles tend to stick together even when suspended in air. This can be rectified by treating the powder with dichloridimethylsilane to render its surfaces hydrophobic (Al-Chalabi *et al.*, 1990). Dichloridimethylsilane chemisorbs to SiO_4 tetrahedra exposed along silicate surfaces. Another affective hydrophobic agent for use with silicates is the commercial surfactant Teepol. Hydrophobic surfactants, however, will cause severe flocculation of all mineral particles in water (Kaye and Davis, 1962).

1.5.5.2.1 Lower particle size limit of chemical dispersion

The repulsive potential between similarly charged surfaces remains constant as particle size decreases. However, particles smaller than 0.1 μm will always flocculate, despite the presence of a deflocculant (van Olphen, 1977). The reason offered here for this phenomenon is that when the sizes of particles decrease, their Brownian movement is enhanced (see Eq. 1.5.1.1.2.1). Hence, collisions between increasingly smaller particles become more severe, so that double layer repulsion is overcome, and flocculation takes place.

1.5.5.3 Influence of clay particle shape on flocculation

It is suggested that the distinct platy shape of clay mineral particles should also contribute to its larger tendency to flocculate than is the case with sub-spherical particles. Particle borders of adjacent sub-spherical mineral particles curve away from each other in all directions; hence, van der Waals attraction will diminish exponentially with the sideways increase in surface-to-surface distance (section 1.5.5.1.2). The attractional forces, however, between two parallel flat clay surfaces are constant along the whole of their lengths, and should therefore be much higher. This, along with a higher net surface charge, and its dual nature, should be one of the main reasons why clays flocculate much more readily than other mineral particles.

1.5.6 Consequence of deflocculant hydrolysis on clay surfaces

Due to its high electric charge, clay surfaces can act as catalysts in chemical reactions (Schmidt, 1976). It is also known that with the ageing of kaolinite suspensions dispersed with a sodium polyphosphate (Calgon and TSP), the suspensions can become unstable due to the hydrolysis of deflocculant molecules, which is catalysed by the clay surfaces (Lyons, 1990).

Sodium polyphosphates adsorbed on clay surfaces undergo slow hydrolysis to form orthophosphate – a process moderately accelerated by a decrease in pH (Green, 1950). In kaolinite suspensions, sodium polyphosphate already exhibits some hydrolysis within 6 hours (Michaels, 1958). Hydrolysis is highest with montmorillonite, followed by kaolinite, while goethite-induced hydrolysis was significantly lower. With all minerals, their coarser fractions (2-20 μm) induced more hydrolysis than their finer fractions (0.2-2 μm). At 28 days, the hydrolysis was still in progress. The rates of hydrolysis also grew with an increase in temperature from 10-30 °C.

During this study an investigation was therefore merited to see how long it would take before hydrolysis will affect the accuracy of particle size analysis results with each of the deflocculants used (section 4.2.3.1).

1.5.7 Potential negative effects related to clay properties during sample preparation

During sample preparation, the natural clay samples are converted to such a form that particle size analysis can be conducted as far as possible on single mineral particles, thus ensuring accuracy. To effect this, a number of sample preparation methods are employed prior to particle size analysis (Jackson, 1968; Gee and Bauder, 1986; Allen, 1995). Clay particles, however, have unique characteristics that during the execution of some of these preparatory steps can defeat their very purpose. These characteristics are: a thin platy shape, a perfect {001} cleavage and, for smectites, an open crystal structure due to swelling in water.

All of the sample preparation methods, in one way or the other, serve to break mineral assemblies down to single particles. Mineral assemblies can be in the form of flocks, agglomerates, or the more resistant aggregates. These three types of mineral assemblies differ from each other according to mechanical strength.

Flocks are loose assemblies of single particles, sticking together due to attractional electrostatic forces in water. Hence, flocks have the smallest mechanical strength, and can be dismantled only by using a deflocculant and/or a high pH.

However, upon drying, flocks become agglomerates that are stronger composites of clay particles bound together into soft clumps by salt bridges and van der Waals forces (Nelson, 1988). Upon re-suspension, their constituent particles will not be released by deflocculants only. Therefore, prior to particle size analysis, agglomerates have to be broken up by mechanical means *viz.* through grinding in a mortar and pestle, followed by shaking and/or ultrasonic treatment. Break-up is accelerated by the presence of deflocculants (Chappel, 1998;

see also section 4.1.3.2.1).

The third and strongest type of particle assemblages is called aggregates. They have some kind of cement that binds them together. It is either in the form of organic material, different types of oxides, or amorphous coatings on particle surfaces (Jackson, 1968). Amorphous coatings on clay surfaces often become gel-like in water (Ferris and Jepson, 1975), and can act like a glue to stick single particles together.

Before particle size analysis, aggregates must first be broken down by chemical dissolution, and/or grinding by mortar and pestle. Then, any agglomerates that might remain must be broken up by ultrasonic treatment (Jackson, 1968; Kunze and Dixon, 1986; Gee and Bauder, 1986; Sheldric and Wang, 1993 – see also sections 1.5.7.1 and 4.1.3.1).

With chemical dissolution completed, all soluble salts originating from the chemical procedures, and those originally contained in the soil, need to be removed. Otherwise, electrolytes will induce flocculation, undermining accuracy (section 1.5.5.1.2). Dissolved salts are removed by means of vacuum filtration, centrifugal washing, or dialysis (Jackson, 1968, Kunze and Dixon, 1986). During centrifugal washing, flocculation is used to facilitate fast deposition of suspended clay particles. This is achieved by using polar liquids (such as ethanol, acetone or methanol), or heating of the suspension (Jackson, 1968; Kunze and Dixon, 1986 – see also section 4.1.1 and 4.1.1).

For accurate particle size analysis with all sedimentary methods, the samples should not contain particles larger than permitted by Stokes' Law, or permitted by the 100% adjustment of the Sedigraph (Jackson, 1968; sections 1.5.1.1 and 1.4.2). Particles larger than the upper size limit therefore are removed first. This is accomplished by means of dry or wet sieving, or through size fractionation by means of gravitational or centrifugal sedimentation (Jackson, 1968; Allen, 1995).

Next, the bulk samples need to be dried, to allow them to be ground into a fine powder (sections 1.5.7.3 and 4.1.2.3). This enables accurate weighing of samples, which in turn permits constant suspension concentrations, ensuring repeatable and reproducible results.

Being in powder form also enables division of bulk samples by means of a sample splitter into representative sub-samples small enough for Sedigraph analysis (Allen, 1995). Representative smaller samples are essential in providing acceptable repeatability. During the current study, a spinning riffler was used for this purpose. To further insure repeatability, 1 kg bulk samples of each kaolinite type were homogenized beforehand by shaking it up-and-down with a simultaneous circular movement. Then each bulk sample was split into 10 samples of

100 g each. Each of those was again split into 10 samples, thus securing 100 samples of ±10 g each.

After a sample suspension is made up, two further steps are taken to acquire single mineral particles. First, it is deflocculated by means of a chemical dispersant (sections 1.5.5.2, 4.1.2.1 and 4.1.2.2). Finally, the particles are de-agglomerated as far as possible with the help of ultrasonic treatment (sections 1.5.7.4 and 4.1.3.1). If their binding agents allow it, ultrasonic treatment can replace chemical dissolution to break up aggregates (Arustamyants, 1991).

Omitting any of the above procedures, or conducting them improperly, will be detrimental to both the accuracy and reproducibility of size analyses succeeding it. The literature studies on the effects on accuracy of soluble salts, solid concentration, the addition of deflocculants and pH were already discussed under the sections dealing with flocculation and chemical dispersion (sections 1.5.5.1.2 and 1.5.5.2). Then will be presented a literature study disclosing the need for the correct approach to *chemical dissolution*, *grinding by mortar and pestle*, and for *ultrasonic treatment*. The mechanisms of each treatment, and the specific clay characteristics that present the greatest dangers during each, will be discussed. The correct approach to minimize potential detrimental effects to accuracy and reproducibility will also be given.

The magnitude of the effects on accuracy and reproducibility should most of the above sample preparation techniques be conducted incorrectly were also established experimentally. Their test reports can be found in Chapters 4 and 5.

1.5.7.1 Flocculation due to desalination with organic polar liquids

Clays, with predominantly Ca^{2+} the exchange cation, do not disperse well in water after drying (Rengasamy, 1982). After Ca^{2+} is exchanged with Na^{+}, though, dispersivity improves. However, when a Ca^{2+} clay is centrifugally washed with ethanol instead of water, and is *dried* and re-suspended in water, it disperses equally well as Na^{+} clays (Rengasamy, 1982). During ethanol washing, the ethanol molecules replace the strong water-Ca^{2+} bridges between dry clay particle surfaces with weaker hydrogen bonds between adsorbed ethanol molecules, bringing about vastly improved dispersivity.

However, if clay suspensions that are centrifugally washed with ethanol, methanol, or acetone are not dried to evaporate all free polar liquid, the accuracy of the subsequent particle size analysis results is noticeably reduced since free polar liquid molecules acts as flocculants (section 4.1.1).

1.5.7.2 Adverse results of chemical dissolution methods

It is known that kaolinite can be contaminated by hydrated iron oxides (such as limonite [Fe· OH·nH_2O], goethite [FeO·OH]) and hydrated aluminium oxides (such as gibbsite [$Al(OH)_3$, and boemite [AlO(OH)]). They can be present either as free particles of up to 100 Å in diameter, or as an amorphous coating on surfaces of single kaolinite particles (Jefferson *et al.*, 1975; Angel and Vincent, 1978). Amorphous coatings can increase the viscosity of clay slurries, and reduce the efficiency of deflocculants to disperse clay particles (Ferris and Jepson, 1972). Their presence should therefore endanger the accuracy of all particle size analysis methods.

Most detrimental, though, for the accuracy of particle size analysis is the formation of hard aggregates bound together by non-silicate minerals (Chappel, 1998). These are: various amorphous iron oxides such as hematite [Fe2O3] and goethite [FeO·OH], amorphous silica [SiO_2], amorphous alumina [Al_2O_3], and amorphous aluminosilicates (allophane) [Al_2O_3][Si_2O_3]. It can also be crystalline minerals such as: calcium and magnesium carbonates [$CaCO_3$ and $CaMg(CO_3)_2$], pyrolusite [MnO_2], and Gypsum [$CaSO_4$] (Jackson, 1968; Chang and Jackson, 1957; Jackson, 1958; Weaver *et al.*, 1968; Chahi *et al.*, 1996).

Organic surface coatings can equally be present; soils with a carbon content of up to 0.05% are common (Ferris and Jepson, 1972). Due to its low X-ray absorbancy, it is assumed that free organic particles will not seriously affect analyses results. But, organic surface coatings may also bind clay particles into aggregates (Kunze and Dixon, 1986), hence preventing single particle size analysis (Hereter *et al.*, 2002).

If the size analysis of only *single particles* is the aim, then all aggregates must be broken down by the selective removal of the organic material, and amorphous and crystalline minerals with selective chemical dissolution methods. Along with ultrasonic treatment, the removal of cementing materials from clays before particle size analysis is the most important sample preparation step to assure accurate results.

The full procedures to test for, and selectively remove organic matter and the mineral cements are thoroughly described in Jackson (1968), Kunze and Dixon (1986), and Sheldric and Wang (1993). A short summary of each of these methods is as follows:

1. First, test for gypsum by shaking the soil in distilled water. Then add acetone; with gypsum present a white gell will form. Also test the soil suspension for the amount of soluble salts by conductivety measurements (Kunze and Dixon, 1986, for the procedures of both tests). If present, remove gypsum and other soluble salts by

centrifugal washing, retrieving the sample through flocculation by heating the suspensions just prior to centrifugation (Jackson, 1968). Repeat untill both tests for soluble salts are negative.

2. Test for, and remove Ca and Mg carbonates with a sodium acetate buffer, adjusted to pH 5 with acetic acid (either Grossman and Millet, 1961 or Kunze and Dixon, 1986). The alternatively method of Sheldric and Wang (1993) to remove carbonates with the HCl should rather be left alone due to the potential damage to the crystal lattices of clay minerals (Gee and Bauder, 1986).
3. Then test for, and remove organic material and MnO_2 with hydrogen peroxide (H_2O_2) (Kunze and Rich, 1959; Kunze and Dixon, 1986 give the same procedure). When no MnO_2 is present, rather use the NaOBr method for organic matter removal. It provides the largest recovery of fine clay, and the best dispersion for particle size analysis of all methods for organic matter removal, including the H_2O_2 method (Protz and St. Arnaud, 1964).
4. Remove colloidal alumina, colloidal aluminosilicates, and iron oxides with the Na-citrate-bicarbonate-dithionide method (Kunze and Dixon, 1986).

When de-aggregation is accomplished through dissolution of oxides and amorphous cements, it will reduce the ultrasonic time necessary to obtain single clay crystals for particle size analysis since only the weaker agglomerates will then have to be destroyed. This will diminish the potential damage to clay particle due to ultrasonic breakdown, thus producing more accurate results (section 1.5.7.4). With chemical dissolution there are, however, also inherent dangers to the accuracy of all particle size analysis methods.

Potential detrimental effects of dissolution pre-treatment

Apart from removing binding agents, dissolution pre-treatment will also remove soil minerals like gypsum and other soluble salts, MnO_2, Ca and Mg carbonates, and iron oxides, when present as separate grains in a clay sample. This will modify the particle size distribution, depending on the amounts of these minerals present before dissolution.

Dissolution pre-treatment also dissolves some of the crystalline fraction (Kunze and Dixon, 1986). It is assumed here that this will especially be the case for smaller particles, due to their relatively large surface areas. Hence, the amount of smaller particles may be reduced, decreasing their cmp values. Accordingly, the sizes of the remaining particles will be reduced.

Both H_2O_2 and the citrate-bicarbonate-dithionite methods cause 'weathering' of poorly

ordered vermiculite, and vermiculite/montmorillonite mixed-layered clays, due to hydrogen attack, and the removal of inter-layer Al^{3+} (Brewster, 1980). This should shrink the thickness of their particles.

H_2O_2 treatment, furthermore, will exfoliate vermiculite, cause its flotation on water, and hence its subsequent removal during centrifugal washing (Jackson, 1968). This will modify the particle size distribution of the clay fraction according to the amount of vermiculite present in the natural sample before H_2O_2 treatment.

The citrate-bicarbonate-dithionite method of iron oxide dissolution removes some of the inter-layer aluminum material of smectites and vermiculite. This resulted in greater expansion in water, and greater collapse upon K-saturation (Harward and Theisen, 1962; Harward *et al.*, 1962). It is reasonable to assume that this will affect particle sizes, and hence decreases the accuracy of size analyses results.

In contrast, humic substances adsorbed on clay edges, along with the presence of other *free* organic material, increase the stability of kaolinite, montmorillonite, and illite suspensions (Kretzschmar *et al.*, 1993; Tarchitzky *et al.*, 1993; Heil and Sposito; 1993; see also the results of section 4.1.1.1). Hence, H_2O_2 treatment before particle size analysis might even increase the esd values as opposed to that of natural samples.

Due to the potential detrimental effects of dissolution treatment to accuracy, the soundest policy is to first determine which of these binding agents are present, and then to apply only the appropriate chemical pre-treatment as mildly as possible (Harward *et al.*, 1962; Kunze and Dixon, 1986; Whittig and Allardice, 1986).

1.5.7.3 Need for caution during grinding

Preceding any particle size analysis, all clay samples must first be ground down to a powder, with nothing greater than sugar-sized pellets left in it. This is needed to facilitate accurate weighing of the samples to the nearest milligram. When aggregates are too large then accurate weighing to the 3 rd decimal becomes impossible.

Clay minerals should never be mechanically milled in a ball mill or oscillatory mill prior to particle size analysis. Such treatment delaminates, and breaks the clay particles into smaller particle sizes (Alcover and Giese, 1986; Pérez-Rodríguez *et al.*, 1988). Contrarily, dry grinding of kaolinite can even lead to *aggregation*, with the formation of *larger* particles consisting of its finer artefacts (González-García *et al.*, 1991).

Prolonged mechanical grinding can also break and crush the layers parallel to the basal

plane, causing re-arrangement of the co-ordination polyhedra, and transfer of protons within the structure (Stepkovska, 1990). Kaolinite and pyrophyllite damaged in this way, collapse when stored a few days under dry conditions. This would reduce both accuracy and reproducibility.

However, after only 10 min. of oscillatory grinding of kaolinite, it spontaneously delaminates even further to thinner particles when stored at 100% relative humidity. Twenty days of storage after only 5 min. of oscillatory dry grinding has the same detrimental effect (Stepkovska *et al.*, 2001). Prolonged grinding in a ball mill or oscillatory mill may even destroy the kaolinite crystal-structure, changing it to an amorphous mineral (Kristóf *et al.*, 1993).

For these reasons a mortar and pestle must always be used to pulverise clays for particle size analysis. Great care, though, needs to be taken even when using a mortar and pestle. Both the standard methods of the American Standards for Testing and Materials ASTM D2217-1985[6] and ASTM D421-1985[7] prescribes a rubber-coated mortar and pestle, to keep the modification of particle size at a minimum during grinding.

During this study, a porcelain mortar and pestle were used. Enough clay was added to the mortar to always have at least a 2 mm layer of clay powder between mortar and pestle when grinding clay samples. This was done to prevent clay particles being delaminated along cleavage planes by direct contact between the hard surfaces of the two implements. To also keep potential rotational breakage to a minimum, great care was taken to rather grind softly and with patience.

The effects of an incorrect grinding technique on accuracy were experimentally established in section 4.1.3.1.

1.5.7.4 Dangers of ultrasonic pre-treatment

When a liquid is exposed to ultrasonic waves of increasing energy, small bubbles start to appear above a certain threshold value of ultrasonic power. These bubbles are also called cavities, and the process of its formation is called cavitation. An ultrasonically created cavity is considered an area of vacuum that develops due to brief "stretching" of the liquid by the longitudinal, high-energy, sub-sonic waves passing by a fixed point. The amount of cavities

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[6] ASTM D2217-85 (1998) *Standard Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants.*

[7] ASTM D421-85 (1998) *Standard Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants.*

grows with the increase in ultrasonic power (watt) of the ultrasonic vibrator (Johnson *et al.*, 1972).

Cavities collapse again after about 2 µsec., and have a strong impact on any solid material in its close vicinity. Collapse produces local high velocity water jets (± 100 m/sec.), and strong local pressure gradients of approximately 20 GPa/cm^3. The resulting hydrodynamic forces are strong enough to break up particle assemblages that are weakly bonded – such as by van der Waals forces. Stronger bonding, for instance by oxides and amorphous materials, can also be destroyed. The distance over which breakdown is experienced by surrounding aggregates, though, is only about 100 µm (Aoki *et al.*, 1987). However, water jets and pressure gradients may even fracture solid particles that are close enough, modifying their particle size.

The rate of ultrasonic de-aggregation is, amongst others, a function of material properties like surface charge and the strength of binding agent like oxides and amorphous materials. But by and large, the rate of break-up depends on the amount of ultrasonic time, and ultrasonic energy (watt). Ultimately, it is the total amount of ultrasonic energy that determines the complete break-up of agglomerates and aggregates (Kusters *et al.*, 1994). Therefore, it is surmised that if the ultrasonic power is higher, the time to fully break up all aggregates will be shorter. But, if the same amount of ultrasonic energy is expended at lower watt but longer duration, the amount of aggregate break-up will be the same.

Using ultrasonic probes, both Watson (1970) and North (1976) found that when the duration of ultrasonic treatment of soils was increased, the clay concentration increased, and finally levelled off in a single cmp plateau after about 40 min. (section 4.1.3.1). North interpreted the first, quick rise to the cmp plateau as the break-up of "micro-aggregates" into < 2 µm sub-complexes. The slow rise thereafter, he saw as the subsequent break-up of these < 2 µm sub-complexes into primary particles. During the first part of ultrasonic agglomerate/aggregate break-up, single particles are released, which will then re-agglomerate – just to be broken up again (Malysa and Warzynski, 1995). Break-up finally wins if ultrasonic energy is high enough, and applied long enough.

The smaller the constituent particles of aggregates, the more ultrasonic energy is required to break up the aggregates containing them. Additionally, the smaller the aggregates become, the more energy is required for its break-up (Higashitani *et al.*, 1993). The break-up process also slows down due to the increasing reduction in the amount of projections and corners of the aggregates due to cavitation erosion. This is since most cavitation bubbles form on projections, corners, and micro-cracks. Hence, as these are eroded away, cavitation slows down, and the aggregate break-up is also retarded (Fridman, 1972; see also section 4.1.3.1).

Apart from material properties, time, and watt, there are a number of other factors also *enhancing the efficiency* of ultrasonic break-up of aggregates:

- an increase in *frequency* (Hz.) (Arustamyants, 1991),
- a decrease in *solids content* (Saly, 1967; Edwards and Bremner, 1967; Bonfils and Dupuis, 1969),
- an increase in *salt concentration* (Hinds and Lowe (1980) – but below the critical coagulation concentration, otherwise flocculation results (Higashitani *et al.*, 1993),
- a decrease of the *volume of liquid* in ultrasonic baths (Walmsley and Williams, 1991),
- a decrease in the *volume of sample suspension* (Walmsley and Williams, 1991),
- a decrease in *viscosity* of the suspension liquid, and the ultrasonic bath liquid (Fridman, 1972),
- a reduction of *liquid pressure* with decreasing *depth* in the container (Fridman, 1972),
- a lowering of the *temperature* and the *gas content* of the suspension (Sirotyuk, 1966).
- during this study, ultrasonic treatment was carried out in the presence of the *deflocculant* since the fragmentation of agglomerates is enhanced by its presence (Arustamyants, 1991; Chappel, 1998 – see also section 4.1.2.1). The rate of fragmentation increases with increase in deflocculant concentration (Malysa and Warzynski, 1995).

Potential detrimental effects of ultrasonic treatment on accuracy

Due to the crystal structure, and the extended swelling of some clay types, single clay particles under ultrasonic treatment are much more susceptible to size reduction than other minerals. Due to their {001} cleavage planes, particle delamination can easily take place under sonication (Sudo and Shimoda, 1978). The risk for this should increase, as the amount of swelling of these minerals increases.

Edwards and Bremner (1967) found that soft mineral particles such as biotite mica are abraded by ultrasonic treatment, and are therefore reduced in size. Hinds *et al.* (1996) observed the same for vermiculite particles. Na-montmorillonite sonified at 25 kHz for only 1 min. delaminates into thin flakes. After 15 min. of further ultrasonic treatment, they are broken down to much smaller sizes (Roberson *et al.*, 1968, Sudo and Shimoda, 1978).

Sonication can also cause cavitation erosion on clay mineral surfaces. Three stages are noticed: first the removal of surface contaminants, as noticed for kaolinite by Koms'ka *et al.* (1966). Ultrasonic treatment can damage the very thin amorphous coatings on some clay

mineral surfaces (Jones and Uehara, 1973). A second stage of cavitation erosion is reported by Gâtâ (1964) involving the splitting of the crystal lattice on clay surfaces, accompanied by changes in the X-ray diffraction (XRD) patterns, and an increase in cation-exchange capacity. The last stage of cavitation erosion is the complete fragmentation of the existing crystal structure on clay particle surfaces, and their regrouping into new mineral aggregates along their fresh-formed surfaces (Kruglitskii *et al.*, 1966).

Hinds *et al.* (1996) found that even harder mineral particles like quartz, microcline, and dolomite also showed signs of abrasion after 30-60 min. of sonication. Even the relatively low energy ultrasonic bath can modify the quartz size distribution due to breakage of grains, thus also producing smaller artefacts (Adams and Steward, 1969; Walker and Hutka, 1973; Busacca *et al.*, 1984; McTainsh and Duhaylunsod, 1989). Porter (1962), and Chappel (1998) also found evidence of ultrasonic damage to quartz grain surfaces due to cavitation erosion and particle break-up.

From all of the above it can be concluded that abraded particles will be reduced in size, with a simultaneous decrease in the cmps below their original esds. However, the cmp values below the smaller particles sizes, containing the resultant artefacts, will be enlarged. Hence, the very tool intended to break up soft agglomerates and flocks to obtain a more accurate size analysis of single particles, will actually lead to inaccuracy by further breakage of the single grains.

Contrarily, it was demonstrated that under ultrasonic treatment hydromica clay and palygorskite clay might *coagulate* to *increase the particle size*. Palygorskite also demonstrates a second mechanism of increase in particle size under sonication: with further increase in ultrasonic time, palygorskite progressively undergoes a phase change to form montmorillonite of incomplete crystal structure (Kruglitskii *et al.*, 1966). This should noticeably modify the particle size due to the swelling of montmorillonite.

It must lastly be noted that ultrasound is used extensively for sonochemistry – which is the polymerisation and de-polymerisation of macromolecules (Mason and Lorimer, 1988). From this is surmised that it should be possible that the stronger ultrasonic probes might polymerise or de-polymerise deflocculant polymers. This might reduce its deflocculation efficiency, and compromise the accuracy of subsequent particle size analyses.

All the minerals mentioned above that are abraded by ultrasonic treatment are present in most soils. Hence, great care must be taken when using ultrasonic treatment in sample preparation. An experiment to find the optimum conditions for ultrasonic treatment of clay

minerals, micas and quartz and other harder minerals ahead of particle size analysis is therefore needed (see section 4.1.3.1).

1.5.8 Adverse effects of the presence of swell-clays

Using any sedimentary method with clays, the most important sample-related parameter is the presence of significant amounts of swell-clays (smectites and/or mixed-layered clays). A number of swell-clays attributes can have an adverse effect on accuracy and reproducibility.

Firstly, most montmorillonite particles are concentrated in the smallest size fractions. Brownian diffusion could therefore affect the accuracy of clay analyses when containing substantial amounts of this clay type.

Furthermore, all swell-clays exhibit variable amounts of swelling during particle size analysis, and their amount of crystal layers can reversibly change. Both these mechanisms determine swell-clay particle size in water. Swelling and the amount of crystal layers depend on a variety of chemical and physical conditions. The specific conditions of the natural situation will not necessarily be known; and those that are known, will not necessarily be obtainable during an analysis.

Swelling additionally prevents the accurate determination of the density of swell-clays in water. Therefore, the particle size of swell-clays cannot be calculated accurately with Stokes' Law. When samples consist of a mixture of clays, each with a different clay density, a further density problem is encountered during all sedimentary methods. When analysing such a sample, an average density must be used to calculate particle size. But, when the density of a specific component of a mixture differs greatly from that of the chosen average density, then its particle sizes will be calculated inaccurately.

In the next few sections the various chemical and physical conditions that can change the montmorillonite particle size will be discussed in terms of their effects on accuracy and repeatability. The significance of clay-swelling to the accuracy of all sedimentary methods will also be given. Then, the reason why swelling should present a problem to pycnometric density determinations of swell-clays will be discussed. A novel method will be presented to calculate the density of montmorillonite in distilled water and in air, for a number of interlayer cations. Lastly, the correct way to calculate the average density for clay mixture analyses is provided.

1.5.8.1 The very small particle size of montmorillonite

In most samples, but not all, montmorillonite particles abundantly reside in the below 0.08 µm size fraction (Jackson, 1968). Hence, most montmorillonite particles will *indefinitely stay in suspension* due to Brownian diffusion. Furthermore, most of the rest of its particles will still be below the minimum particle size for sedimentary particle size analysis (0.56 µm). The settling velocity of most of the larger fraction will therefore be retarded by Brownian diffusion (sections 1.5.1.1.2 and 1.5.1.2). These particles will therefore be registered at too small esds, showing too high cmp values.

Furthermore, all particles below 0.1 µm in size will automatically flocculate – *even in the presence of a deflocculant* (section 1.5.5.2.1). Added to that, if a suspension has a large particle size range, containing substantial amounts of very small particles, flocculation is also enhanced. Hence, when enough small-sized montmorillonite particles are present in mixtures with other clay types, stability should be reduced.

It is therefore concluded that, due to montmorillonite's susceptibility to Brownian diffusion and flocculation, accuracy should be compromised during any sedimentary method when its is present in substantial amounts.

1.5.8.2 Change in clay particle size due to swelling and shrinkage

Sedimentary particle size analysis of clay minerals is conducted in water. But in water, smectites and mixed-layer minerals swell along their c-axis due to the uptake of inter-layer water (Hofmann *et al.*, 1933). Since a sedimentary particle size analysis is conducted in water, the sizes measured for swell-clay particles will therefore be different from those when in dry soil.

In the next few sections the physical and chemical factors that modify the particle size due to swelling will be discussed; and where appropriate, their combined effect will be illustrated.

1.5.8.2.1 Extent of swelling related to interlayer cation type, humidity and salt concentration

Montmorillonite in its fully collapsed dried-out state will have a d_{001} spacing that varies between 9.5 Å – 10.0 Å depending on the exchangeable inter-layer cation (Green-Kelly, 1953). When dried out at 200 °C, the d_{001} spacing is very close to the calculated van der Waals thickness of 9.36 Å for a single crystal sheet (Hofmann and Klemen, 1950). However, in *air*, the d_{001} spacing is always more than that due to the uptake of ever-present water vapour. In water, the swelling is even larger.

The amount of swelling firstly depends on the nature of the inter-layer cation, and the

relative humidity (RH) (Norrish, 1954). When *in air*, the amount of layers of absorbed water increases as the RH increases. Interlayer cations with larger charge densities usually cause larger swelling. When in *water*, the amount of swelling therefore depends on the inter-layer cation type, and also on the concentration of *any* cation in solution (Mattson, 1929a, b). The lower the concentration of dissolved cations, the larger the swelling in water. The largest expansion of all occurs in distilled water (Mattson, 1929a, b; 1931a, b, 1932; Falconer and Mattson, 1933).

Inter-layer cations can be exchanged by other cation species, by suspending a swell-clay in a strong solution of that cation type (Mattson, 1929a, b). Thus, swelling related to this factor can be regulated.

With most inter-layer cations (i.e. Cs^+, NH^{4+}, K^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, and Al^{3+}), the amount of swelling for montmorillonite is of similar magnitude – regardless of whether in air, at 100% RH, or suspended in water. With all of these interlayer cations, montmorillonite has d_{001} spacings below 20Å. The exception to the rule, though, is when Na^+, Li^+, and H^+ are the montmorillonite exchange cations. When suspended in weak salt concentrations in water, swelling with these cations are much larger than when in air at 100% humidity. In distilled water, Na^+-, Li^+-, and H^+-montmorillonite d_{001} spacings can expand up to 400 Å in water, while in air it only reaches a maximum of 17.0 Å (Norrish, 1954; Fu *et al.*, 1990).

Therefore, depending on the type of inter-layer cation, there are two orders of magnitude of swelling for montmorillonite. With the first mentioned interlayer cations, the particle volume increases to less than 2x its dry volume. However, the larger order of swelling with Na^+-, Li^+, and H^+ interlayer cations increases the particle volume with up to 20-30x (Norrish, 1954).

From the above it is clear that when size analyses are conducted in distilled water by any method, the determined particle sizes of montmorillonite should differ immensely from what it in reality has in its dry state in soil. Besides this, the magnitude of this difference can vary hugely. Variation depends, amongst others, on the interlayer cation type, and the humidity while still in the dry state, and salt concentration when in water. For this reason a summary of the amount of montmorillonite swelling under these conditions is supplied below.

A) Inter-layer cations associated with small increases in montmorillonite particle size (< 2x expansion):

In *air* the order of magnitude of swelling for the inter-layer cations causing small expansions is: $Cs^+ < K^+ < Mg^{2+} < Ba^{2+} < Ca^{2+}$ (Table 1.5.8.2.1.1 (a)). However, in *water* the order is slightly different: $Cs^+ < NH^{4+} < K+ < Ba^{2+} < Ca^{2+} < Mg^{2+} < Al^{3+}$ (Table 1.5.8.2.1.1 (b).

From the order of swelling of these cations, it can be seen that the smaller the cation radius generally becomes, and the larger the cationic charge, the larger the swelling. This should be due to an accompanying increase in cation charge density down the order.

Larger charge densities will increase the amount of water molecules hydrating the inter-layer cations. As a consequence, the thickness of the interstitial water layer increases (Mooney *et al.*, 1952; Norrish, 1954).

The d_{001} spacings of montmorillonite with different inter-layer cations, and their percentage increase in volume in air and water, is summarised in Tables 1.5.8.2.1 (a) and (b), respectively. Literature references are also supplied.

Table 1.5.8.2.1.1 (a). The increase in particle size of montmorillonite in *air* for the most common exchange cations causing less than 20 Å swelling, at various relative humidities.

Exchange Cation	RH	d_{001}	Number of Water Layers	% Increase in Particle Volume	Reference
Cs^+	0%	10.4 Å	0		Mooney *et al.*, 1952
	60 - 100%	12.6 Å	1	21%	"
$K^+_{(synth.\ clay)}$	0-95%	10.0 Å	0		"
	70-100%	12.6 Å	1	26%	"
$Mg^{2+}_{(synth.\ clay)}$	0%	13.9 Å	Random*		Tamura *et al.*, 2000
	60-90%	15.8 Å	2	14%	"
	90-100%	18.5 Å	3	33%	"
Ba^{2+}	0%	10.4 Å	0		Mooney *et al.*, 1952
	17-50%	12.7 Å	1	22%	"
	68-100%	16.7 Å	2	61%	"
$Ca^{2+}_{(synth.\ clay)}$	0-10%	11.9 Å	1		Tamura *et al.*, 2000
	60-95%	15.2 Å	2	28%	"
	90-100%	18.1 Å	3	52%	"
Ca^{2+}	0%	10.2 Å	0		Mooney *et al.*, 1952
	48-78%	15.4 Å	2	51%	"
	90-100%	16.7 Å	3	64%	"

- Random means an inter-layer spacing associated with an irrational d_{001} series.

Table 1.5.8.21 (b). The increase in particle size of montmorillonite in *water* of the most common exchange cations causing less than 20 Å swelling, at various salt concentrations

Exchange Cation Salt	Salt Concentration	d_{001}	Number of Water Layers	% Increase in Particle Volume	Reference
CsCl	Dried out	10.0 Å	0		Norrish, 1954
	0.7 N	13.4 Å	Random*	34%	"
	Dist. H_2O	13.8 Å	Random	38%	"
NH_4Cl	Dried out	10.0 Å	0		"
	4.0 N	14.3 Å	Random	43%	"
	0.2 N - Dist. H_2O	15.0 Å	2	50%	"
KCl	Dried out	10.0 Å	0		"
	4.0 N	12.7 Å	1	27%	"
	0.2 N - Dist. H_2O	15.0 Å	2	50%	"
$BaCl_2$	Dried out	9.8 Å	0		"
	2.0 N	18.7 Å	Random	91%	"
	Dist. H_2O	18.9 Å	3	93%	"
$CaCl_2$	Dried out	9.5 Å	0		"
	8.0-1.0 N	15.4 Å	2	62%	Slade and Quirk, 1991
	Dist. H_2O	18.9 Å	3	100%	Norrish, 1954
$MgCl_2$	Dried out	9.5 Å	0		"
	8.0-1.0 N	16.2 Å	2	71%	Slade and Quirk, 1991
	Dist. H_2O	19.2 Å	3	102%	Norrish, 1954
$Al_2(SO_4)_3$	Dried out	9.5 Å	0		"
	0.1 N - Dist. H_2O	19.4 Å	3	104%	"

* Random means an inter-layer spacing associated with an irrational d_{001} series.

B) Inter-layer cations associated with large increases in montmorillonite particle size (> 30x expansion):

In *air*, Li^+-montmorillonite can swell between 21% – 50% as humidity increases, whereas the Na^+ variant expands by between 27% – 72% (Table 1.5.8.2.2 (a)).

In *water*, the least amount of swelling is with the H^+-montmorillonite variety: at a strong 16 – 2.7N concentration of $H^+(H_3O+)$, its swells by 54%. But, with all three the H^+, Na^+, and Li^+-montmorillonite varieties, as salt content is decreased towards distilled water, the particle volume increases by a huge 3078% and more (Table 1.5.8.2.2 (b)).

Table 1.5.8.2.2 (a). The increase in particle size of montmorillonite in air for Na^+, and Li^+ at various relative humidities.

Exchange Cation	RH	d_{001}	Number of Water Layers	% Increase in particle volume	Reference
$Li^+_{synth.}$	0 - 30%	10.1 Å	0		Tamura *et al.*, 2000
	0 - 70%	12.2 Å	1	21%	"
	40 - 100%	15.1 Å	2	50%	"
Na^+	0%	9.9 Å	0		Gillery, 1959
	20 - 42%	12.6 Å	1	27%	"
	68 - 83%	15.5 Å	2	57%	"
	83 - 100%	17.0 Å	2	72%	"

Table 1.5.8.2.2 (b). The increase in particle size of montmorillonite in water for Na^+, Li^+, and H^+ at various salt concentrations

Exchange Cation Salt	Salt Conc.	d_{001}	Number of Water Layers	% Increase in Part. Vol.	Reference
NaCl	Dried out	9.5 Å	0		Mering, 1946; Barshad, 1950; Norrish and Quirk, 1954; Norrish, 1954
	4.0-1.6 N	15.4 Å	2	62%	
	1.6-0.28 N	18.9 Å	3	99%	
	0.3 N	18.9 - 40.0 Å*	Unknown	321%	Mering, 1946
	0.01 N	133 Å*	Unknown	1300%	"
	< 0.01 N	190 Å*	Unknown	1900%	"
	Dist. H_2O	300 Å+*	Unknown	3078%+	Falconer and Mattson, 1933; Norrish, 1954
LiCl	Dried out	9.5 Å	0		Norrish, 1954
	16-2.7 N	15.4 Å	2	62%	
	2.7-1.0 N	19.0 Å	3	100%	
	1.0-0.8 N	22.5 Å	4	137%	
	0.66 N	31.0 Å*	Unknown	226%	
	0.01 N	135 Å*	Unknown	1321%	
	Dist. H_2O	300 Å+*	Unknown	3078%+	
$H^+(H_3O^+)$	Dried out	10.0 Å	0		Norrish, 1954
	16-2.7 N	15.4 Å	2	54%	
	2.7-1.0 N	19.0 Å	3	90%	
	1.0-0.8 N	22.4Å	4	124%	
	0.66 N	31.0 Å*	Unknown	210%	
	0.01 N	115 Å*	Unknown	1050%	
	Dist. H_2O	300 Å+*	Unknown	2900%+	

* Diffuse diffraction peaks

Lastly, when Li^{+}-, Mg^{2+}-, Al^{3+}-montmorillonite are heated to over 200 °C, 300 °C, and 400 °C, respectively, they collapse to a $d_{001} \approx 9.5$ Å (González-García, 1950; Green-Kelly, 1953; White, 1956; Brindley and Ertem, 1971; Jaynes and Bigham, 1987, Chorom and Rengasamy, 1996). At these temperatures, Li^{+}, Mg^{2+}, and Al^{3+} migrate from the interlayer spaces to vacant octahedral positions, neutralising excess (–) charge. All of them thus develop hydrophobic unit-layer surfaces, and therefore their capacity for swelling is irreversibly destroyed. Hydrophobic surfaces additionally lead to severe flocculation in water (Chorom and Rengasamy, 1996).

1.5.8.2.2 Modification of swelling by chemical deflocculants

Norrish (1954) observed increased Na-montmorillonite swelling upon adding Calgon (a sodium polymetaphosphate deflocculant) to a montmorillonite suspension. At a low salt concentration of 0.05N NaCl, an acid-treated montmorillonite swelled to a basal spacing of 23 Å. However, after Calgon addition, it swelled to 48 Å (a 109% increase in particle volume).

Raussell-Colom (1958) and van Olphen (1961b) ascribed edge to face associations of vertical montmorillonite unit-layers, cross linking to horizontal unit-layers, as the force that limits swelling additional to van der Waals forces (Fig. 1.5.8.2.2.1). When the (+) edge-charges are reversed to (–) by a dispersant, then the edge-to-faces association is broken, and swelling increases (van Olphen, 1961b).

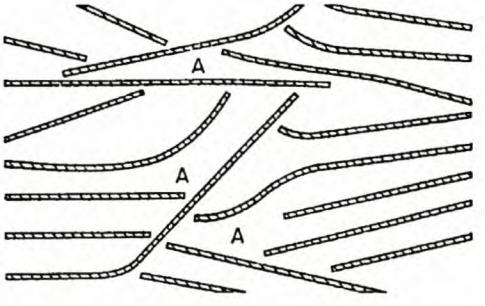

Fig. 1.5.8.2.2.1. Edge to face cross-linking to explain increased swelling of montmorillonite due to deflocculation with chemical dispersants (after van Olphen, 1961b).

Norrish (1954) also found that after desalinating his suspension above, the shrinkage during a subsequent salt treatment became more reversible when also adding a sodium polymetaphosphate deflocculant. Without a deflocculant, cross-linking apparently limited re-swelling when the salt concentration of the desalinated suspension was increased again.

Findings of Norrish and Rausell-Colom (1961) seemingly confirm the cross-linking theory. Their XRD analysis of montmorillonite showed that increasing the pH to above that of the p.z.c. also lead to increased swelling (also see section 1.5.8.2.3). It is concluded here that at this pH range, edge-charges will be reversed to negative, which will also break up the inferred edge to face associations causing cross linking.

By using data of Morvan *et al.* (1994), the magnitude of Na-montmorillonite swelling in the presence of a deflocculant, as during particle size analysis, can be calculated. They added Dispex (Na-polyacrylate deflocculant) to Na-montmorillonite samples for XRD analysis. Their results show that the magnitude of swelling increase, when both the solids and Dispex concentrations are lowered. From their results it is calculated here that for a solid concentration of about 0.38% by volume, and a deflocculant concentration the same as that for particle size analysis (1.5%), the d_{001} spacing of *Na-montmorillonite* will be 563 Å. This represents an increase in particle volume of 88% above that in distilled water.

An alternative explanation is suggested here for the increased Na-montmorillonite swelling with a deflocculant. The highly charged polyanions might move into the wide-open inter-layer spaces, and adsorb to (+) charges of the inter-layer surfaces. The outwardly orientating deflocculant charges will greatly increase the total (−) surface charge. Therefore, more cations (hydrated by water dipoles) will be needed to neutralise the inter-layer surface charge, causing the observed increase in swelling when a deflocculant is added.

This view can be proven if it is found that substantially less sodium hexametaphosphate remains in solution in Na-montmorillonite suspensions, than in (say) an illite suspension. If Na-montmorillonite can absorb deflocculant molecules between its crystal layers, it will remove more deflocculant from solution than the non-swelling illite would. However, illite has a 1½ times larger surface charge density than montmorillonite (van Olphen, 1977). Therefore, if no deflocculant is absorbed into Na-montmorillonite, then illite suspensions should remove more of it, since then only surface adoption is possible for both.

In stark contrast with Na-montmorillonite, *Ca-montmorillonite* collapsed completely to a d_{001} of about 9.5 Å at a 2.8% Dispex concentration (Morvan *et al.*, 1994). It represents a 50% decrease in particle volume as compared to that in distilled water. This is also to be expected during particle size analysis since a 2.8% Dispex concentration is of the same order of magnitude as that during particle size analysis (1.5%, section 4.1.2.1). To explain the collapse, the authors postulated de-sorption of the interlayer Ca^{2+} due to complexation by the highly charged polyanions in solution.

However, when the same authors increased the deflocculant concentration to above a critical value, Ca-montmorillonite swelled again to give huge d_{001} spacings – similar to those of Na-montmorillonite in the presence of a deflocculant. During sedimentary particle size analysis in water plus deflocculant the d_{001} will therefore be about 563 Å. Their explanation is that at high Dispex concentrations, the amount of dissolved Na^+ is also increased. Hence, the exchange equilibrium becomes favourable for Na^+ to take the empty places of desorbed Ca^{2+} in the interlayer space: causing the observed huge increase in swelling.

This critical deflocculant concentration, however, is much higher than is normally used to deflocculate clay suspensions during particle size analysis. By using the values of these authors, the Dispex concentration to cause the Na-type swelling of Ca-montmorillonite at the typical solids content for Sedigraph analysis is calculated here at approximately 17.26%. However, sedimentary size analysis of clays is done at much lower deflocculant concentrations of around 1.5%. It is therefore concluded that when Ca-montmorillonite is deflocculated during sedimentary size analysis, it will collapse to the smaller particle size and higher density of its fully dried out state (a d_{001} of 9.5 Å, at density 3.0 g/cm^3). Hence, during any sedimentary method, the particle size of Ca-montmorillonite must be calculated by using 3.0 g/cm^3 as the clay density.

1.5.8.2.3 Different swelling with change in pH and salt concentration

At any given salt concentration, Na-montmorillonite at high pH values (pH 6-11) gives a notably larger swelling, and therefore much larger particle sizes than at lower pH values (Norrish and Raussell-Colom, 1961).

Furthermore, the salt concentration and pH has a synergistic effect on particle size. As the salt concentration is decreased, the difference in particle size between acidic and alkaline Na-montmorillonite samples becomes larger. At a 0.25 N NaCl concentration, the sample pre-treated at pH 1-6 swelled to 42 Å, as opposed to the 54 Å at pH 6-11 (a 29% larger volume). At an even lower NaCl concentration of 0.02 N NaCl, the pH 1-6 sample swelled to 94 Å, while the pH 6-11 sample gave a much larger swelling at 137 Å (a 46% larger volume) (Norrish and Rausell-Colom, 1961). In both cases, the samples were still flocculated. Upon further lowering of the salt concentration to below 0.02 N, the alkaline samples began to disperse (Norrish and Rausell-Colom, 1961).

However, when these authors added a *deflocculant* to a slightly salty Na-montmorillonite suspension, the swelling increased about one order of magnitude above when dispersing it by

only using an alkaline pH. At a 0.25 N NaCl concentration, a Na-montmorillonite sample dispersed with Calgon swelled to 63 Å. This represents a 50% increase in particle volume, as opposed to the 29% increase when it was dispersed above in distilled water at pH 6-11. When adding a deflocculant at an even lower salt concentration of 0.02 N – as might occur during particle size analysis – the d_{001} spacing increased to 187 Å. This represents a 99% increase in particle volume, as opposed to the 46% increase also at pH 6-11 but without a deflocculant.

The last two sections clearly demonstrate the diverse effects on swell-clay particle size when dispersing it only by desalination and increasing the pH, and/or by the addition of a deflocculant.

1.5.8.2.4 Change in swelling with change in solid concentration

Hight *et al.* (1962) showed with small angle X-ray scattering that a decrease in solids content of Na-montmorillonite in distilled water, leads to a sharp increase in d_{001} spacing. When their experimental values are used, a Na-montmorillonite d_{001} spacing of about 300 Å is calculated for the solid concentration of the Sedigraph (3.85% by volume) in distilled water. Hence, when particle size analysis is conducted at the typically lower solid concentrations of 0.6% with the Andreasen method, then the particle sizes of Na-montmorillonite will be even larger than in the Sedigraph.

1.5.8.2.5 Variation in swelling due to differences in isomorphous substitution

Swelling is also partly a material function: it decreases with the increase in surface charge density of the unit-layer surfaces. The higher the surface charge, the lower the salt concentration needed for a clay to swell to the same d_{001} spacing (Slade and Quirk, 1991). From this can be concluded that the particle size of a particular type of swell-clay should vary according to the amount of isomorphous substitution in its tetrahedral and octahedral positions.

1.5.8.2.6 Control on swelling by outside pressure

The magnitude of swelling is limited by positive outside pressure, and increased by negative outside pressure (Falconer and Mattson, 1933). From this can be concluded that the swelling of any particular clay type should decrease with increasing soil overburden, as well as with increasing water pressure as soil depth below the water table is increased.

1.5.8.2.7 Change in the amount of swelling with change in temperature

When the soil temperature rises, evaporation will increase the relative humidity in its open pore spaces. This will increase the swelling. Therefore the particle size in dry soil will vary with soil temperature and distance to the water table.

However, the same phenomenon does not occur with a temperature rise in *water* – which is the condition in which most sedimentary particle size analysis is conducted. Therefore the actual particle size at different temperatures in soil can not be reproduced during sedimentary particle size analysis. Especially the Na-, Li- and H-montmorillonites will give large differences with that when in soil since, depending on the RH in dry soil pore spaces, it can swell up to 33x - 57x more in water in the presence of deflocculants than in air (sections 1.5.8.2. and 1.5.8.2.2).

1.5.8.3 Variations in swell-clay particle size due to change in the amount of unit-layers

Besides swelling, a change in the amount of unit-layers can also modify the particle size of swell-clays (van Olphen, 1950b). As with swelling, this change depends on a number of chemical and physical factors – some of which are the same as those that control the amount of swelling (section 1.5.8.2). In relation for most of these factors the amount of unit-layers is reversible.

Each of these factors, and their effects on swell-clay particle size, are discussed in the next few sections.

1.5.8.3.1 Amount of crystal layers related to type and concentration of the exchangeable cation

As with swelling, the amount of unit-layers comprising a montmorillonite particle differs with the type and concentration of the exchangeable interlayer cation in suspension.

In dilute suspensions, montmorillonite plates form stacks of parallel-oriented particles called quasi-crystals or tactoids. Like the amount of swelling, the amount of unit-layers of a montmorillonite quasi-crystal will also vary according to the *type* of the exchange cation (Banin and Lahav, 1968; Whalley and Mullins, 1991).

When studying the findings of the above authors, it is concluded that the number of unit-layers per crystal increases in the order $Li^+ < Na^+ < K^+ < Mg^{++} < Ca^{++}$. Note that for these cations, the order of the magnitude of *inter-layer swelling* is virtually the opposite (section 1.5.8.2.1). Li^+ for instance, will have less unit-layers but will swell more, whereas the opposite

is increasingly true along the order for the amount of unit-layers. The balance of these two effects will cause the actual particle size; at the Li^+ end, swelling should dominating (swell of 300 Å and more in distilled water).

When montmorillonite suspensions contain both Ca^{2+} and Na^+ ions in solution, and the inter-layer Na^+ exceeds 20%, the clay particles start to break down into thinner crystals. But when Na^+ had replaced 60% of the absorbed Ca^{2+}, the particles separate into single unit-layers (Shainberg and Otoh, 1968).

Shainberg and Kaiserman (1969) furthermore found that when more than 10% by weight Na-montmorillonite powder is added to a Ca-montmorillonite suspension, the particle size also starts to decrease. When 70% by weight of Na-montmorillonite is added, the Ca-montmorillonite particles separate into single unit-layers. It is concluded here that this is due to the migration of some of the inter-layer Na^+ to exchange the inter-layer Ca^{2+}. When 60% of the Ca^{2+} had been replaced, it causes unit-layer separation. Shainberg and Kaiserman found the opposite effect when Ca-montmorillonite was added to Na-montmorillonite suspensions.

To complicate matters even further, the increase in concentration of the exchange cation, leads to a smaller particle size, due to a decrease in swelling (section 1.5.8.2.1). In contrast, however, the increase in Ca^{++} concentration will simultaneously cause the opposite, by increasing the number of unit-layers of Ca-montmorillonite (Dufey and Banin, 1979). The particle size in relation to the type and concentration of the exchange cation will be a balance between the opposite effects of swelling and the amount of crystal layers.

1.5.8.3.2 Change in the amount of crystal layers with change in solid concentration

A change in the solid concentration similarly has opposite effects on the amount of swelling and the amount of unit-layers. Hight *et al.* (1962) showed that increasing the solid concentration leads to *less* swelling (section 1.5.8.2.4), but simultaneously the amount of unit-layers is increased. At 40% solids by weight Na-montmorillonite had 3-5 unit-layers per tactoid, and a d_{001} spacing of 32 Å. However, when the solids were increased to 85%, the d_{001} spacing reduced to 13 Å. In addition to this, van Olphen (1950b) found with various techniques that with an increase in solid concentration, the average *thickness* of both Ca- and Na-montmorillonites particles *enlarges* due to an increase in the amount of unit-layers. Hence, when increasing the solid concentration, the effect of addition of unit-layers on the particle size overshadows the effect of reduced swelling.

Moreover, an increase in solid concentration will also lead to increased flocculation

(section 1.5.5.1.2), thereby adding to the increase in the particle size.

1.5.8.3.3 The amount of crystal layers in relation to external pressure and pressure history

By solving the Scherrer equation for the basal XRD reflections of Ca-montmorillonite, Blackmore and Miller (1961) determined the average amount of unit-layers before and after pressure was applied. They found that after applying 100 atm. outside-pressure, the average amount of unit-layers per crystal increased irreversibly from 4.5 to about 8 unit-layers.

1.5.8.3.4 Change in the amount of crystal layers with ageing

When increasing the salt content of any clay suspension to above the so-called critical coagulation concentration (c.c.c.), the clay platelets will flocculate.

When Hight *et al.* (1962) increased the NaCl, $CaCl_2$, and $AlCl_3$ concentrations of Na-montmorillonite 2% suspensions to above their c.c.c., they discovered that flocks consisted of face-to-face associations. Tactoids had between 6 to 8 unit-layers, with inter-layer spacings of between 19-21 Å (114 Å – 168 Å in total crystallite thickness). But upon ageing for 4 months, the particle sizes decreased to a total crystallite thickness of 44 Å – 72 Å. The cause was found to be a decrease in the number of unit-layer platelets to 2-3 per particle – despite an increase in d_{001} spacings of between 22-24 Å. Therefore, like with the increase in solid concentration, the effect of the amount of crystal layers during ageing once again overshadow that of swelling.

1.5.8.4 Density determinations of swell-clays

In the fully collapsed dried-out state, montmorillonite has a density of approximately 3.00 g/cm^3 (Deer *et al.,* 1966). However, water absorbed during swelling is of much lower density than the solid swell-clay unit-layers (3 g/cm^3 for the solid unit layers *vs.* 1-1.8 g/cm^3 for water – the water density decreases as swelling increases) (Boek *et al.*, 1995; Deer *et al.*, 1966). It is therefore concluded here that as swelling increases, the densities of smectites and mixed-layer clay particles should decrease.

To calculate particle size with a sedimentary method, the accurate density of the particles must be known (see Stokes Law: Eq. 1.4.1.1). With the Andreasen method, the density is needed to calculate the sedimentation time for every chosen particle size to reach the extraction-depth from the top of the suspension. For the Sedigraph, clay density is needed to calculate the scan rate.

It is, however, not possible to experimentally determine the density of a swollen clay. Due

to the uptake of intra-crystalline water, none of the pycnometric methods can be used to accurately determine the density of swell-clays.

1.5.8.4.1 Problems with Pycnometric density determinations of swell-clays

Should the density of single smectites be determined experimentally, it must be done under the same conditions as during a sedimentary particle size analysis. Therefore, the clay particles must be fully swollen in distilled water, and in the presence of a deflocculant (section 1.5.8.2.2). Hence, the liquid pycnometric method must be used, with distilled water as the liquid plus a deflocculant at same concentration as during particle size analysis.

With the liquid pycnometric method, the volume of a *dry* powder of known mass is determined in any liquid, who's density is known at the temperature of determination (ISO 787-10:1993, ISO 8130-3:1992 and ISO 1014:1985 [8]; ASTM D854-02; Blake and Hartge, 1986). From its experimentally determined mass and volume, the powder density is calculated.

However, to give an accurate volume of swollen clay particles, all of the liquid added to the pycnometer needs to stay outside and enclosing *already swollen* clay particles (unit-layers plus water). However, with this method, when the water is added to the dry clay, it will be partially outside the clay minerals, and partially be absorbed into it. Therefore, the added water will totally enclose each of the solid unit-layers, and not only the outside of already swollen clay particles as it should. The clay volume thus determined will be the volume of the dry clay, and not its swollen volume required to give its swollen density (the density of unit-layers plus already absorbed water). Instead, the calculated density of the swell-clay will be its dry density.

Moreover, for swell-clays with exchange cations causing swelling less than 20 Å, interstitial water has a larger density than normal water, and its density increases the smaller the d_{001} spacings becomes (Karaborni *et al.*, 1996). This causes an inaccurate water density that is used to calculate the volume, which in turn is used to calculate the dry density. Therefore, the dry density calculated in the above way will not be accurate either.

To alleviate the above problem, already swollen particles could theoretically be used. But

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[8] *ISO 787-10:1993 General methods of test for pigments and extenders -- Part 10: Determination of density -- Pyknometer method*

ISO 8130-3:1992 Coating powders -- Part 3: Determination of density by liquid displacement pyknometer

ASTM D854-02 Standard Test Methods for Specific Gravity of Soil Solids by Water Pycnometer

ISO 1014:1985 Coke -- Determination of true relative density, apparent relative density and porosity

then, the mass of the *swollen* clay particles is needed, which is also impossible to obtain. To be fully swollen, the individual clay particles must be completely surrounded by water, therefore in a fully saturated watery paste. Hence, weighing it in its fully swollen state will give a higher mass than the exact mass of the swollen particles containing only their *interstitial* water.

A gas pycnometer cannot be used to determine the *swollen* density of swell-clays either. When determining the clay particle volume, the clay-filled gas pycnometer needs to be completely evacuated before gas is allowed into it (ISO 8130-2:1992 [9]). Under such high vacuum, all of the interstitial water will be removed from inter-layer spaces, ultimately also giving the dry density. Proof of this is that during the XRD analysis of swell-clays at a 0% RH, the swell-clay particles completely collapses to a d_{001} spacing close to that of a single unit-layer (section 1.5.8.2).

For these reasons, it is concluded that the density determined by any pycnometric method will always differ from the true swollen density in water and in humid air. Hence, the particle sizes of *swell-clays* are always calculated incorrectly when using any sedimentary method. This problem was solved for swell-clays in distilled water and in air, by devising a novel method to calculate the swollen density from Monte Carlo data obtained from the literature.

1.5.8.4.2 Calculating the density of montmorillonite in water from Monte Carlo data

To calculate the density of any swell-clay in distilled water and air, a new formula was derived. It makes use of the relationship between the dry clay density and the density when fully swollen in distilled water. This relationship, in turn, is proportional to the relationship between the d_{001} spacing in the dry state and that in the fully swollen state; and the density when fully swollen is proportional to the density of the interstitial water.

The dry mass can be obtained by weighing, and since the density is known (3.00 g/cm^3) (Deer *et al.*, 1966), the dry volume can be calculated. Both the d_{001} spacings are determined by means of XRD, and the density of interstitial water for each interlayer cation can be calculated by means of Monte Carlo simulations. Keeping all of these in mind, the formula was derived. as follows:

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[9] *ISO 8130-2:1992 Coating powders -- Part 2: Determination of density by gas comparison pyknometer (referee method)*

The dry density (ρ_{dr}) of a swell-clay is given by:

$$\rho_{dr} = \frac{m_{dr}}{V_{dr}} \qquad \text{Eq. 1.5.8.4.2.1}$$

with m_{dr} the dry mass, and V_{dr} the dry volume of the clay in its collapsed state.

Similarly, the swollen density (ρ_{sw}) of a swell-clay is given by:

$$\rho_{sw} = \frac{m_{sw}}{V_{sw}} \qquad \text{Eq. 1.5.8.4.2.2}$$

where m_{sw} is the total mass of the swollen clay ($m_{dr} + m_{iH_2O}$), and V_{sw} the total volume of the swollen clay ($V_{dr} + V_{iH_2O}$), with m_{iH_20} and V_{iH_20}, respectively, the mass and volume of the interstitial water in the swollen state. Therefore Eq. 1.5.8.4.2.2 can be rewritten:

$$\rho_{sw} = \frac{m_{dr} + m_{iH_20}}{V_{dr} + V_{iH_2o}} \qquad \text{Eq. 1.5.8.4.2.3}$$

Furthermore, the amount of increase in volume with swelling is defined here as the swell-factor (S), where:

$$S = \frac{V_{sw}}{V_{dr}}$$

But since the increase in volume during swelling is directly proportional to the increase in d_{001} spacing, therefore:

$$S = \frac{V_{sw}}{V_{dr}} = \frac{d_{001\ \textit{fully swollen}}}{d_{001\ \textit{fully collapsed}}} \qquad \text{Eq. 1.5.8.4.2.4}$$

If the fully collapsed dry volume (V_{dr}) is now taken as 1 cm^3, then first of all Eq. 1.5.8.4.2.1 becomes:

$$\rho_{dr} = \frac{m_{dr}}{V_{dr}} = \frac{m_{dr}}{1} = m_{dr} \qquad \text{Eq. 1.5.8.4.2.5}$$

And secondly, Eq. 1.5.8.4.2.4 becomes:

$$S = \frac{V_{sw}}{V_{dr}} = \frac{V_{sw}}{1} = V_{sw}$$

But $V_{sw} = V_{dr} + V_{iH_2O}$, therefore, when the 1 cm^3 of dry clay (V_{dr}) has fully swollen then:

$$S = V_{sw} = V_{dr} + V_{iH_20} = 1 + V_{iH_20} \qquad \text{Eq. 1.5.8.4.2.6}$$

Therefore, the volume of interstitial water V_{iH_20} of the clay when swollen is given by:

$$V_{iH_20} = S - 1 \qquad \text{Eq. 1.5.8.4.2.7}$$

But the density of the interstitial water ρ_{iH_2O} of the swollen clay are calculated as follows:

$$\rho_{iH_2O} = \frac{m_{iH_20}}{V_{iH_20}}$$

where m_{iH_20} is the mass of interstitial water. Therefore:

$$m_{iH_20} = \rho_{iH_20} \times V_{iH_20} \qquad \text{Eq. 1.5.8.4.2.8}$$

Insert Eq. 1.5.8.4.2.6 into Eq. 1.5.8.4.2.7, which then becomes:

$$m_{iH_20} = \rho_{iH_20} \times (S - 1) \qquad \text{Eq. 1.5.8.4.2.9}$$

By inserting Eq. 1.5.8.4.2.5, 1.5.8.4.2.6, and 1.5.8.4.2.9 into Eq. 1.5.8.4.2.3, the swollen density of a 1 cm^3 of swell-clay (ρ_{sw}) can be calculated by the following formula:

$$\rho_{sw} = \frac{\rho_{dr} + (\rho_{iH_2O} \times (S - 1))}{S} \qquad \text{Eq. 1.5.8.4.2.10}$$

The swell-factor *S* is calculated with Eq. 1.5.8.4.2.4 using the d_{001} in the fully collapsed dried out state, along with the d_{001} in the swollen state. The dry density is determined by weighing, after drying the swell-clay overnight at not more than 110 °C. The density of the interstitial water for every exchange cation type (ρ_{iH_2O}) is obtained by a Monte Carlo simulation.

Monte Carlo simulations are the modern approach to obtain the exact spatial arrangement between the inter-layer cations, the water molecules hydrating them, and the atoms of swell-clays (Bleam, 1993; Sposito *et al.*, 1999). It comprises the simulation of the equilibrium molecular structures of liquids molecules and the atoms of solids. It is obtained by combining all the available knowledge of quantum chemistry, statistical mechanics, electrostatic theory, and crystal chemistry by means of a super computer. Monte Carlo simulations are also used to shed more light on the swelling mechanism with the different exchange cations.

To obtain the density of interstitial water the following formula is used (Boek *et al.*, 1995):

$$\rho_{iH_2O}(N) = \frac{Nm_{H_2O}}{V(N) - V(0)} \qquad \text{Eq. 1.5.8.4.2.11}$$

with $V(N)$ the volume of the super-cell of a swell-clay that contains N water molecules per super-cell, $V(0)$ the volume of the super-cell in the fully collapsed state, and m_{H_2O} is the mass in gram of one water molecule. A clay super-cell in this calculation consists of 8 crystallographic unit cells. A Monte Carlo simulation can be conducted for any interlayer cation, and gives the amount of water molecules per super-cell (N) and the super-cell dimensions in the xy crystallographic plane. The z-dimension is the d_{001} spacing which, for the fully collapsed state, and is also obtainable from the Monte Carlo simulation. The z-dimension for the fully swollen state for the given interlayer cation is obtained from XRD data. With all of these known, $V(N)$ and $V(0)$ can be calculated, and then used in Eq. 1.5.8.4.2.11 to calculated the density of the intestinal water. Finally, with this known, the swell-clay density can be calculated with Eq. 1.5.8.4.2.10.

The ρ_{iH_2O} for *Na-montmorillonite* was obtained directly from the Monte Carlo simulation of Boek *et al.* (1995). Their simulation shows that, after the first water layer containing 48 water molecules is completed (d_{001} = 12.6 Å), the interstitial water density reaches 1.25 g/cm^3. However, the interstitial water density quickly drops to vary with further swelling just above and below 1 g/cm^3. For Li-montmorillonite, the change in inter-layer water density follows the same pattern. Therefore, after the Na-form swells past d_{001} = 12.6 Å, and the Li-form past 12.2 Å, the inter-layer water density of both can be taken as the same as the bulk density of water at ±1 g/cm^3.

With the inter-layer water density known (1 g/cm^3), the density of Na-montmorillonite in pure water (ρ_{sw}) can now be calculated by means of Eq. 1.5.8.4.2.10. Na-montmorillonite expands from 9.5 Å in the dry state to 300 Å in its fully swollen state at the solid concentration of Sedigraph analysis (section 1.5.8.2.4). Therefore:

$$S = \frac{300}{9.5} = 31.57$$

In its fully dried out state the clay density (ρ_d) is 3.00 g/cm^3. Therefore, 1 cm^3 of Na^+-montmorillonite will have a dry mass (m_d) of 3 g. When these values are inserted into Eq. 1.5.8.4.2.10, a density for Na^+-montmorillonite fully swollen in water of 1.0634 g/cm^3 is obtained. For H- and Li-montmorillonite in the fully swollen state, the clay density will be the

same, since in distilled water it gives the same order of swelling (Table 1.5.8.2.2 (b)).

The above result of the novel formula can be tested by using the experimental data of Antipov-Karataev (1939). They determined that fully swollen Na-montmorillonite absorbs 10 grams of water per 1 gram of dry clay. Using these figures, along with the density of water as 1 g/cm^3, and the density of the solid portion of montmorillonite as 3 g/cm^3, the swollen clay density is calculated here as follows:

One gram of dry clay, with density 3 g/cm^3, has a volume of $m_d/\rho_d = {}^1/_3 = 0.33333$ cm^3. The 10 g of absorbed water has a volume of approximately 10 cm^3. Hence, after it has swollen, the one gram of clay will have a total particle volume (v) of 10 + 0.33333 = 10.33333 cm^3, and will weigh 11 grams (m).

Therefore the swollen density will be ρ_{sw} = m/v = 11/10.33333 = 1.0645 g/cm^3. This is very close to the swollen density of 1.0634 g/cm^3 calculated by means of Eq. 1.5.8.4.2.10 – confirming its validity.

In the presence of 1.5 % Dispex – the deflocculant concentration of particle size analysis – Na-montmorillonite swells to approximately 563 Å (section 1.5.8.2.2). Using Eq. 1.5.8.4.2.10, the swollen density of Na-montmorillonite during particle size analysis is calculated at 1.0337 g/cm^3.

The other cation exchange forms of montmorillonite – *viz.* the K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cs^+, NH_4^+ and Al^{3+} forms – will at most increase only 2x in volume when added to water (Table 1.5.8.2.1 (b)). Their swollen densities will still be lower due to swelling, since the inter-layer water will still be less dense than the solid mineral unit-layers. The swollen densities will, however, not decrease as dramatically as with the Na^+-, Li^+-, and H^+-forms. This will reduce the negative effects on accuracy related to Brownian diffusion, and the difference with the average clay density when mixtures are analysed. Therefore, prior cation exchange with either K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cs^+, NH_4^+ or Al^{3+} cations will partially solve the problem of extreme montmorillonite swelling.

Since all of the latter exchange cation causes limited swelling below 25 Å, the density of the interstitial water associated with them will be higher than that for bulk water (Karaborni *et al.*, 1996). The Monte Carlo simulation for *K-montmorillonite* (Boek *et al.*, 1995) established an interstitial water density of 1.3 g/cm^3 at the maximum swollen state in distilled water (d_{001} = 15.4 Å). By using Eq. 1.5.8.4.2.10, the swollen density for the K-montmorillonite can be calculated at approximately 2.35 g/cm^3.

For *Ca-montmorillonite* the density of the interstitial water was calculated by re-working the Monte Carlo data of Greaterhouse and Storm (2002). Their super-cell also consisted of 8 unit cells, and its dimensions in the *xy* crystallographic plane are 21.12 Å x 18.28 Å. The *z*-dimension is the d_{001} spacing, which for the fully collapsed state was calculated by their simulation at 10.4 Å, and for the fully swollen state at 16.6 Å.

The above dimensions gives a super-cell volume for the fully collapsed state V (0) = 4.0152 x 10^{-21} cm^3, and that for the fully swollen state V (N) = 6.4088 x 10^{-21} cm^3. The mass, furthermore, of a water molecule is calculated at 2.991 x 10^{-23} g. With 96 water molecules needed in the inter-layer space per super-cell to achieve the fully swollen state, the density of the interstitial water is calculated at 1.1996 g/cm^3 (Eq. 1.5.8.4.2.10). Then using Eq. 1.5.8.4.2.10 the Ca-montmorillonite clay density in the fully swollen state in distilled water is calculated at 2.08 g/cm^3. However, in the presence of a deflocculant Ca-montmorillonite collapses completely to a density of 3.00 g/cm^3 (section 1.5.8.2.2).

Dispersing a swell-clay suspension can theoretically be achieved in *distilled water* by only using a pH higher than that at the p.z.c. at the edges (pH 7). As will be seen in the following section 1.5.8.2.2, a particle size analysis of Ca- and Na-montmorillonite should not be determined while dispersed by a chemical deflocculant, since the latter severely modifies the particle size. Therefore, with the ability to obtain the swollen densities in distilled water, sedimentary particle size analysis of Na-, Li-, H-, Ca-, and K-montmorillonites can now be attempted by using only desalination and high pH (section 4.1.2.3). The following swollen density values can be used: 1.063 g/cm^3 for Na-, Li, and H-montmorillonite, 2.08 g/cm^3 for Ca-montmorillonite, and 2.35 g/cm^3 for K-montmorillonite.

However, in the presence of Dispex, a density of 1.0337 g/cm^3 must be used for Na-montmorillonite, and for Ca-montmorillonite 3.00 g/cm^3.

Similar Monte Carlo simulations were not found for the exchange cations Mg^{2+} and Al^{3+}. They are the most common exchange cations after Ca^{2+}, Na^+, and K^+ to be found in nature. Therefore, it is not yet possible to, in like manner, calculate swollen densities for Mg^{2+}- and Al^{3+}-montmorillonite.

There is third way whereby the swollen density can be calculated. If the mass of the absorbed water is known, the amount of water molecules per super-cell can be calculated by making use of the following: When approximately 0.1g H_2O is added to 1 g dry clay, it corresponds to 23 water molecules per super-cell (Newman, 1987). Similarly, with their Monte Carlo simulation Boek *et al.* (1995) calculated 0.1002 g H_2O for every 23 water

molecules in Li-montmorillonite, 0.0980 g /23 water molecules for Na-montmorillonite, and 0.0960 g for K-montmorillonite. If the latter three are averaged, it gives a value of 0.098 g H_2O per 23 interstitial water molecules – which corresponds closely to the value of Newman (1987). The mass of water absorbed by 1g of dry clay ($m_{abs.H_2O}$) to cause swelling at any measured d_{001} spacing can be experimentally obtained by the method either of Falconer and Mattson (1933) or Antipov-Karataev (1939). Using all the aforementioned, the following formula is derived to calculate the amount of water molecules (N) per super-cell:

$$N = \frac{m_{abs.H_2O}}{0.1} \times 23 \qquad \text{Eq. 1.5.8.4.2.12}$$

With N known, the density of the intestinal water can be calculated with Eq. 1.5.8.4.2.11, where after the swell-clay density can be obtained through Eq. 1.5.8.4.2.10.

As in the case with distilled water, clays holding very small salt concentrations can be dispersed for particle size analysis by increasing the pH to above that at the p.z.c. at the clay edges (section 1.5.5.2). However, if enough salt is present swelling will be less, and the swollen densities of Na-, Ca-, and K-montmorillonite will be higher than those calculated above from their Monte Carlo data. However, Monte Carlo simulations for montmorillonite published up to now, only represents the addition of water molecules to the inter-layer space when the ambient humidity is increased; but the effect of ionic strength on the addition of inter-layer water when suspended in water is not taken in account. From this it is surmised that clay densities cannot as yet be calculated for different salt concentrations, until the amount of interstitial water layers in relation to the salt concentration is also taken in account during Monte Carlo simulations. Therefore, the sedimentary particle size analysis of Na-, Ca-, and K-montmorillonite can, as yet, only be attempted at high pH, in distilled water.

When air classification is used, the swell-clay density at any RH can also be calculated in the same way as that in distilled water. Firstly, the d_{001} spacing is determined with XRD analysis at the relevant RH. According to the d_{001} spacing and the interlayer cation type, the amount of water layers at the relevant RH is roughly obtained from Tables 1.5.8.2.1 (a) and 1.5.8.2.2 (a), or directly from the Monte Carlo simulation. Finally the inter-layer water density is calculated, which is then used to calculate the swell-clay density at the specific RH in air.

1.5.9 Inaccuracy caused by the presence of mixed-layered clays

Some clays have basic unit-layers consisting of different clay mineral species that are stacked face to face to form their particles. Such clay particles mostly consist of combinations of varying amounts and orderings of different smectites, illite, and kaolinite. They also combine with other clay types such as vermiculite, and other plate silicates such as chlorite. This phenomenon is called interstratification (I/S), and these clays are called mixed-layered clays.

Mixed-layered clay particles can be formed by natural processes in rock (Hendricks and Teller 1942; MacEwan, 1956, 1958; Środoń *et al.*, 1990; Dong and Peacor, 1996; Kasama *et al.*, 2001). In rock, illite/montmorillonite mixed-layered clays are interpreted as being the product of incomplete alteration of montmorillonite to illite due to diagenesis, or hydrothermal action (Hower *et al.*, 1976; Shau *et al.*, 1989; Dong and Peacor, 1996). Montmorillonite/ kaolinite interstratified clays can also be found in nature, but are very rare (Sudo and Shimoda, 1978; Altschuler *et al.*, 1963; Schultz *et al.*, 1971).

However, mixed-layered clays can also be produced artificially in a manner that should be very detrimental to the accuracy of particle size analysis. Suspensions consisting of mixtures of illite plus swell-clays (especially montmorillonite), can be transformed into mixed-layered minerals through agitation (Nadeau *et al.*, 1984a, b; Nadeau, 1999). This is especially the case with the Na^+ or Li^+ forms of montmorillonite. Due to extended swelling, they delaminate along their water inter-layers during any type of mechanical action. Then, montmorillonite unit-layers combine with illite, to form crystallites consisting of "fundamental particles" of one or more 20 Å unit-layers of illite, randomly interstratified by "fundamental particles" of single 9.5 Å unit-layers of montmorillonite.

The larger the amount of montmorillonite fundamental particles present in mixed-layered mineral crystals, the thicker they are (Środoń *et al.*, 1992; Kasama *et al.*, 2001). Therefore, the more montmorillonite present in an agitated salty suspension of different clay types, and the higher the solid concentration, the larger the resultant mixed-layered particle sizes should be after sample preparation.

Środoń and Elsass (1994) also found that the ease of formation of illite/montmorillonite-interstratified systems also depends on geometric factors. Suspended mixed layer particle components coagulate more easily if they have flat surfaces, large diameters, and are not elongated. From this is deduced that the larger the diameter of the single clay types in a mixed

clay suspension, the greater the ease of I/S formation during sample preparation.

Apart from the above effects, it is obvious that mixed-layer clay minerals will also cause most of the same problems during any particle size analysis method in water, as the single swell-clays (sections 1.5.8.1 to 1.5.8.4) These are: the increase in particle size due to swelling, the change in the number of fundamental units, and the unknown swollen density.

Summary and conclusions on the effects of mixed-layered clays:

1. The spontaneous increase in amount of unit-layers due to various reasons (section 1.5.8.2.7), confirms the ease with which mixed layer clay formation may inadvertently be produced when suspending natural clay samples in water during sample preparation. Therefore the particle size distribution of clay mixtures containing swell-clays (smectites and mixed-layered minerals) will always depend on the size of the original particles in suspension, and the combination of all the factors controlling the amount of unit-layers, *i.e.* type and concentration of the exchange cation in solution, solid concentration, pressure history, and ageing (section 1.5.8.2.7).
2. Mixed-layered clays generally have larger crystals, called "mega-crystals" (Ahn and Peacor, 1986), or "quasi-crystals" (Środoń *et al.*, 1990). This implies that the formation of mixed-layered minerals during sample preparation should increase the particle sizes above that of their original components.
3. Na^+-montmorillonite can be split along basal cleavage planes due to ultrasonic treatment (section 1.5.7.4). Hence, smaller particle sizes are artificially produced. In addition, like all other clays, its surfaces can be damaged by ultrasonic treatment. The same should happen along the montmorillonite components of mixed-layered clay minerals.
4. During cation exchange of single swell-clays or clay mixtures prior to any particle size analysis, great care must be taken to agitate as softly as possible. Agitation can form either smaller or larger mixed-layered particles (especially with the Na^+- and Li^+-forms). Under cation exchange, even pure montmorillonite particles can re-agglomerate along basal surfaces (sections 1.5.8.3.1 and 1.5.8.3.2). Depending on the solid concentration and the nature of the exchange cation, this may form new mixed-layered particles that are larger, or montmorillonite particles that are smaller than it was before cation exchange.
5. A chemical deflocculant should rather be avoided when working with clay mixtures containing any swell-clays (smectites or mixed-layered minerals). This is firstly to prevent modification of particle size due to delamination and re-combination, and also to avoid the

inhibition of swelling for the Ca^{2+}-form. This affirms the need to attempt particle size analysis without a deflocculant, and to disperse the suspension by only desalination and the increase of pH to above that at the p.z.c. of the edges (section 4.1.2.3).

6. The swollen density of mixed-layered clays is impossible to determine experimentally, or to calculate from Monte Carlo data, since different individual particles consist of random combinations of different clay types. Each particle of the same size will therefore have different densities due to different relative amounts of components, and therefore also due to different amounts of swelling. A sedimentary particle size distribution of swell-clays will therefore always be inaccurate, since the densities of its particles will deviate widely from the average density chosen to calculate the settling velocity.

Recommendations for further study:

Determine the magnitude of the effects of agitation and ultrasonic treatment on the accuracy of particle size analysis of different types of swell-clays by means of sedimentary particle size analysis, augmented by a TEM and XRD study. This must be conducted on suspensions with different solids contents, exchange cation types and concentrations, pH, and deflocculants.

1.5.10 Inaccuracy of clay mixtures containing swell-clays

Most of the abovementioned attributes of smectites and mixed-layer clays will cause the same type of inaccuracies to clay mixtures containing them, as when analysed as single mineral species. For instance, the small sized, and low density Na-montmorillonite fraction of a mixture will stay in suspension because of Brownian diffusion, and due to its a small density difference with water. This will cause too high cmp values for the mixture – especially in the smaller particle sizes. However, since interstratified clays have larger particle sizes, they should not cause the latter problems related to small size.

An additional problem with mixtures is that only one average density can be chosen to calculate its particle sizes; but its constituents have densities that differ from the chosen density. The larger the density difference of components with the chosen density, the less accurate the results will be. When planning to analyse a mixture of clay minerals, the first question therefore always is: which density is to be used to calculate the particle size distribution? Estimating the average density of the mixture according to the densities of its constituents seems like a solution. For all diameters above 0.2 μm, the average density-value

normally chosen for this purpose is 2.65 g/cm^3 (Jackson, 1968).

Chandrasekhar (1994) theoretically determined that noticeable errors are encountered when an average density is used during the sedimentary particle size analysis of mixtures of different mineral types. He used the following formula to calculate the error at any given particle size:

$$\Delta d_1 = \left(\sqrt{\frac{\rho_{s1} - \rho_l}{\rho_{avg} - \rho_l}} - 1 \right) D \qquad \text{Eq. 1.5.10.1}$$

where Δd_1 is the error in particle size for component 1, at particle size D, whereas ρ_{s1} is the density of solid component one, ρ_l is the suspension-liquid density, and:

$$\rho_{avg} = \rho_{s1}\, v_1 + \rho_{s2}\, v_2 + \ldots\ldots \qquad \text{Eq. 1.5.10.2}$$

where v_1 ($v_{2\ldots}$ etc.) is the volume fractions of the components.

Jackson's value above was calculated by averaging the densities of the most common soils-silicates. However, when Eq. 1.5.10.1 is inspected, it is clear that Jackson's value for average density is a simplification, and should therefore not be accurate. It does not take in account the volume fractions of the clay components of the mixture, which varies widely according to particle density. The effect of this can be seen in Table 1.5.10.1, where the densities of clay mixtures are calculated with Eq. 1.5.10.2. The density, for instance, of a mixture containing ⅓ Na-montmorillonite is calculated at 1.753 g/cm^3, which is 34% smaller than Jackson's average value. At the operational temperature of the Sedigraph (35 °C), this density error will cause the esd for the Na-montmorillonite component in that mixture to be calculated 32.3% smaller than it really is (Eq. 1.4.1.6). For Serina filler it's the cmp below 2 µm will be 4.11% larger than it should be (Table 1.5.10.1).

The more the densities of a component differs from the average, the inaccurately wider the particle size distribution for mixtures becomes, and the more the whole particle size distribution of the mixture shifts to larger particle sizes (Chandrasekhar, 1994). Therefore, it is very important to find the correct average density value for a mixture.

Table 1.5.10.1. The difference between the conventional average clay density of 2.65 g/cm^3, and the more accurate average clay densities of different theoretical clay mixtures

CLAY MASS FRACTION OF EACH MIXTURE COMPONENT				
Montm.	**Illite**	**Kaolinite**		
0.75	0.20	0.05		
0.05	0.75	0.20		
0.33	0.33	0.33		
0.20	0.05	0.75		
CLAY VOLUME FRACTION OF EACH MIXTURE COMPONENT			**CLAY MIXTURE DENSITY** (g/cm3)	**ERROR IN CMP WHEN USING 2.65g/cc**
Ca-Montm. (3.00 g/cm3)	**Ca-Illite** (2.75 g/cm3)	**Ca-Kaolinite** (2.63 g/cm3)		
0.73	0.21	0.06	2.926	-1.506
0.05	0.75	0.21	2.736	-0.478
0.31	0.34	0.35	2.785	-0.759
0.18	0.05	0.77	2.703	-0.311
CLAY VOLUME FRACTION OF EACH MIXTURE COMPONENT			**CLAY MIXTURE DENSITY** (g/cm3)	**ERROR IN CMP WHEN USING 2.65g/cc**
Na-Montm. (1.034 g/cm3)	**Na-Illite** (2.75 g/cm3)	**Na-Kaolinite** (2.63 g/cm3)		
0.89	0.09	0.02	1.224	6.335
0.12	0.69	0.19	2.518	0.613
0.57	0.21	0.22	1.753	4.114
0.39	0.04	0.57	2.013	2.959

Surprisingly, Chandrasekhar (1994) also found that this error enlarges, as the percentage of the mineral fraction that differs from that of the other components *decreases*. This is confirmed by the calculations of Bernhardt (1984). He theoretically determined at what percentages of different mixture components the accuracy of sedimentary methods becomes sensitive to the density differences between components. Quartz (σ_s = 2.5 g/cm^3), for instance, has a density that is 47.6% of that of haematite (σ_s = 5.25 g/cm^3). The particle size analysis results of a mixture consisting of them become noticeably inaccurate when the mass percentage of any one component is below 10%. Swollen Na-montmorillonite (1,063 g/cm^3)

has a density of about 41% of that of kaolinite. It is therefore concluded that a noticeable error can also be expected when either of them makes up less than 10% of the total of a mixture of them.

Additionally, the differences in X-ray mass absorption coefficients (μ_m) between minerals in a mixture with different densities, also affects the accuracy of the Sedigraph (Bernhardt, 1984). The error in cmp will be over 1% if the component with the smallest μ_m is over 5%, or when the component with the larger μ_m is over 1%. Therefore, only due to the X-ray measurement system of the Sedigraph, additional errors will be caused by differences in density between the clay components in a mixture.

A further problem is caused for the particle size analysis results of clay mixtures when enough salt is present to cause flocculation (even in the presence of a deflocculant). Mixed-layered minerals will only be formed through agitation when the surface charge density of the different clay species is of similar order of magnitude. But, when the variation in charge density is large enough, then different clay species will be flocculated selectively at different salt concentrations. Beidellite (charge density 13.0 $\mu C/cm^2$) will already flocculate at 0.005-0.007 moles Na^+/litre, whereas montmorillonite (charge density 9.6-11.3 $\mu C/cm^2$) will only flocculate at between 0.008-0.015 moles Na^+/litre (Frey and Lagaly, 1978, 1979).

Moreover, when the salt content of a clay mixture is decreased, smaller particles go into suspension first through spontaneous deflocculation, while larger ones still stay flocculated (Iler, 1975). Hence, selective flocculation and re-suspension the particle size distribution of a specific clay will be determined by its swell-clay composition, and will change as its salt and solid concentrations changes with dilution (see also sections 1.5.8.2.1 and 1.5.8.2.4 and 1.5.8.3.1 and 1.5.8.3.2).

It is furthermore surmised that during a sedimentary analysis, the density problem will be complicated even further if flocculation also takes place. A single flock will be seen as a single particle. The density of such a particle will be determined by the combination of its solid, as well as its liquid components. Due to its typical card-house structure, a flock consisting of clay platelets will enclose a much larger amount of water than flocks of spherical particles. Because of its high water content, a clay flock will have a density close to that of water. Therefore, if an average density of its solid components is used to calculate settling time or scan rate, then flock sizes will be calculated very inaccurately.

It is lastly concluded that due to the interstitial water of Na-montmorillonite, an increase in its content will decrease the density of flocks even further. Although flocks with a high Na-montmorillonite content (density 1.064 g/cm^3) have a much larger particle size than its single particle kaolinite and illite components, the flocks might even settle slower than single kaolinite and illite particles. Since the recorded esds will in fact be that of flocks and not single particles, the recorded particle size distribution should give a very untrue picture of the clay mixture.

1.6 OTHER FACTORS CONTROLLING ACCURACY AND REPRODUCIBILITY OF ALL METHODS

The terminal settling velocity of all types of particles are reduced by two factors *viz.* the wall effect and electro-viscosity. Both of these effects increase the cmp value at any given esd, and accordingly leads to the underestimation of particle size at any given cmp value.

1.6.1 The magnitude of the wall effect with the Sedigraph

When a sphere falls in a cylindrical tube, which has a diameter 100 times the cross section of the sphere, it will encounter 20% more resistance than if the surrounding walls were situated at infinity (Birkhoff, 1950). The reason is that when a particle falls close enough to a container wall, the fluid streamlines collides against it, and are reflected back onto the particle. The portion of the boundary layer closet to the wall is stationary and also distorts the flow pattern around the particle, with the same result (Allen, 1995). Furthermore, the downward flux of a settling particle plus its own volume of dragged-along fluid creates a balancing counter flux of upwards-moving fluid. The closer to the wall, the smaller the area for counter flux (Di Felice, 1996).

The combination of these three effects causes increased drag on the settling particle, decreasing its terminal settling velocity. This is called the *wall effect*. The closer to a wall, and therefore also the smaller the container, the more the wall effect will be liable to affect the particle size analysis results.

According to the Sedigraph Instruction Manual (1979) the error in esd (ΔD) at any diameter (D) due to the wall effect in the Sedigraph sample cell can be calculated by the following formula:

$$\Delta D = D\left(0.324\ \frac{D}{L}\ \log\left(1+\frac{32L}{9D}\right)\right) \qquad \text{Eq. 1.6.1.1}$$

where the Sedigraph 5000D sample cell thickness is $2L = 0.3175$ cm.

Using the above equation, the errors in esd (ΔD) were calculated for three clay particle sizes within the safe operational size range of the Sedigraph. The errors vary between 0.0028 µm at a 2µm diameter, 0.418 µm at a 30 µm diameter, and 1.049 µm at a 50 µm diameter. This is equivalent to a 0.15% error for 2 µm particles – which is still acceptable. But a 30 µm particle will already encounter an unacceptable 1.39% error, and a 50 µm particle an error of 2.10 %.

1.6.2 Influence of electro-viscosity

When a particle moves under gravity when deflocculated with a Na-polymeric salt, as well as in the presence of any other dissolved salt, its electronic double layer becomes distorted. This leads to the formation of a vertical electrical field of the same form as that which would form should a dipole with a vertical axis be fixed at the centre of the particle. Interaction between the electrical field and the surface charge of the particle opposes its downward sedimentation, which is called electro-viscosity. This might under certain circumstances increase the sedimentation velocity by a few percent (Booth, 1954).

When the terminal settling velocity is altered by electro-viscosity, its magnitude (U'_{st}) is given by the following equation:

$$U'_{st} = U_{st}\left(1+\frac{2m\sigma^2}{\rho_s \eta V k}\right)^{-1} \qquad \text{Eq. 1.6.2.1}$$

with U_{st} the Stokes settling velocity without electro-viscosity, m the total mass of all particles in suspension, σ the surface charge/unit area, ρ_s the density of the particles, η the viscosity of the suspension-liquid, V the volume of the suspension, and k the conductivity of the solution (Dulin and Elton, 1952).

Firstly, since the conductivity of the solution will increase when adding a deflocculant, the terminal settling velocity will be increased during sedimentary particle size analysis. Even a

low ion concentration can already have a substantial influence on accuracy, especially at *small particle sizes* (Pavlik and Sansone, 1973; Sansone and Civic, 1975). The latter authors investigated the difference in particle size between spherical glass beads in water, and those in KCl solutions smaller than 0.1 N. They found a noticeable difference when the particle diameters were around 13 μm. But at the 25 μm particle size, equal results were obtained between the result in water and those in the same set of KCl solutions.

Secondly, Dulin and Elton (1952) observed a 32% increase in sedimentation velocity of 6 μm silica particles when the KCl concentration was increased from 10^{-5} to 10^{-2} *N*. The reason is that the effect of electro-viscosity diminishes as the double layer is depressed by the higher electrolyte concentrations (Sansone and Civic, 1975).

If the salt, however, is a deflocculant, it will increases the surface charge, which will expand the double layer, to increase the effect of electro-viscosity. Confusingly, though, according to Eq. 1.6.2.1 a lower surface charge will reduce the effect of electroviscosity.

The sum therefore of the effects of the increase in conductivity, the widening of the double layer, and the increase in surface charge when adding a deflocculant during particle size analysis, should therefore influence the results – but the magnitude is unknown.

It is lastly evident from Eq. 1.6.2.1 that the effect of electro-viscosity on accuracy will, amongst others, be amplified with the increase in solid concentration (m/V) of the suspension. The effect of electro-viscosity at the solid concentration of the Sedigraph (2-3%) should therefore be higher than with the Andreasen pipette method (< 0.6%).

2. THE CHOICE OF CLAY SAMPLES

In order to determine the sample preparation parameters, as well as the apparatus-related parameters for the Sedigraph, a homogeneous and mono-mineralic clay type was chosen. Samples needed to be homogeneous in particle size to ensure reproducibility when determining the effect of any single parameter. Different clay mineral species, furthermore, exhibit diverse characteristic particle size ranges (Jackson, 1968). Hence, if a clay is also mono-mineralic, the absence of variations in particle size from one sample to the next, associated with a difference in mineral composition, would add to better reproducibility.

In addition, the samples had to be non-swelling, to rule out the already mentioned accuracy problems with swell-clays, mixed-layer clay minerals, and clay mixtures in general (sections 1.5.8 to 1.5.9 and section 1.5.10).

Swell-clays, furthermore, have much weaker {001} cleavage planes, especially after having expanded in water, than for instance is the case with kaolinite. This will cause swell-clay particles to delaminate more easily along its {001} cleavage planes during dry grinding, as well as during the stirring or shaking of the subsequent sample-suspensions. The intensity of the grinding is difficult to control which could lead to varying modification of particle size between different samples of the same swell-clay bearing bulk sample. Additionally, alternating amounts of *newly formed* mixed-layered clay species could artificially be produced due to delamination of swell-clays both during dry grinding, and the agitation of the suspensions following it (section 1.5.9).

If heterogeneous clay samples were used, especially those containing swell-clays, an unpredictable combination of any of the above effects could have brought about the undesirable modification of particle size. This would have concealed the true influence of the single parameter under investigation. On these grounds it was decided to rather use mono-mineralic clay samples. They should also be known to have a small and a constant amount of mineral impurities, and additionally give stable suspensions.

2.1 REASONS FOR USING KAOLINITE

The clay chosen to investigate both the apparatus-related and sample preparation parameters was kaolinite. The reasons were:

1) *Industrial kaolinite is virtually mono-mineralic:*

Of all clay minerals mined on industrial scale, kaolinite is most easily beneficiated to a pure mono-mineralic form. Contrary to all other clay mineral types, some kaolinite deposits contain no, or very little, other clay minerals species. A number of mono-mineralic kaolinites could therefore easily be obtained, and could safely be used to determine the influence on accuracy and reproducibility of the apparatus-related and sample preparation parameters.

2) *A wide choice of industrial kaolinites is available:*

Kaolinite has more applications than the other clay types. Its high demand therefore causes it to be mined in many locations. In contrast, pure montmorillonite is mined on an industrial scale at only one location in South Africa, whereas for illite no such mines exist in South Africa.

3) *Industrially beneficiated kaolinite is usually virtually homogeneous:*

The particle size range and mineral content of kaolinite are kept within tight limits by quality control in beneficiation plants due to the strict requirements for some of the uses (*e.g.* ceramics). This is accomplished by continuously mixing kaolinites from different locations in the deposit at the necessary ratios.

The homogenising effect produced by the processes of the entire large-scale beneficiation process furthermore ensures that the mineral content and particle size distribution of the small 5 kg bulk-samples used during this study was very *homogeneous*. This brought about very good repeatability and reproducibility (section 4.2.2.3.1).

4) *Kaolinites vary little in density:*

Of the more common clay minerals kaolinite has the smallest variation in density (2.61–2.68 g/cm^3, averaging 2.63 g/cm^3). Contrarily, the density of illite fluctuates between 2.6 – 2.9 g/cm^3, and that of montmorillonite between 2.0 –3.0 g/cm^3. Its density amongst others determines the settling velocity, and accordingly also the particle size values of the clay particles. Therefore, when determining the effect of the intentional variation of one parameter in a series of consecutive samples, it is better to

use the clay with the smallest potential density variation.

5) *Kaolinite is easy to disperse:*

Many commercial deflocculants are available to bring about the successful deflocculation of kaolinite in water.

In the case of commercial montmorillonite and mixed-layered clays, large-scale cation exchange is often conducted. However, the excess salts are not removed afterwards. This will lead to flocculation during subsequent particle size analysis in water, despite the presence of a deflocculant. In consequence, to attain accurate analyses results, these salts must be removed by repeated ultra-centrifugal washing or dialysis in distilled water. Industrial kaolinites have low salt contents, and therefore do not need such time-consuming sample preparations.

6) *Kaolinite's size distribution is within the required range for the sedimentary methods for particle size analysis:*

As opposed to smectites or mixed-layered clay minerals, the largest part of the size range of kaolinites falls between the 0.56 - 49.6 μm size limits for all sedimentary of particle size methods (section 1.5.1.1). In contrast, only some montmorillonite clays can be analysed since the *larger part* of their particle size distributions usually fall below the lower size limit of 0.56 μm. Furthermore, due to the flat size distribution of montmorillonites between these two size limits (0.56 - 49.6 μm), small changes caused by the intentional variation of the parameter under investigation will go undetected.

The five kaolinites used to test the magnitude of all of the sample preparation- and apparatus-related parameters were: "Serina filler" and "Serina coater" (Serina Clay Company, Noordhoek, South Africa), "Amazone coater", "Dinkey filler" and "Dinkey coater".

The fineness of Dinkey filler is characterised by a cmp of 52% < 2 μm, for Serina filler it is 60% < 2 μm, Serina coater 78% < 2 μm, Dinkey coater 82% < 2 μm; whereas Amazone coater is the finest at 99% < 2 μm. These specific kaolinites were intentionally chosen due to their increase in fineness. This would enable the establishment of how the resultant increase in total surface area would control the optimum deflocculant concentration for each. The higher the surface area, the more (+) charges, and hence the more deflocculant it should need for complete deflocculation (section 4.1.2.1). It follows that choosing kaolinites with several degrees of fineness allowed obtaining the approximate range of deflocculant concentrations for kaolinites in general.

It was furthermore noticed that these five kaolinites exhibited a fluctuation in dry strength[10]. Hard crushing, needed to break down clay aggregates of higher dry strength, could split appreciable amounts of single clay particles along their {001} cleavage planes. This would cause inaccurate particle size analysis results. Besides this, since the intensity of crushing is difficult to control, the cleavage of single clay particles could also lead to reproducibility problems when comparing samples. An experiment to see whether the intensity of grinding would impinge on accuracy and reproducibility particle size will be discussed under section 4.1.3.1.

Differences in the aggregate strengths of the five kaolinites could in addition have required different durations of preliminary soaking and ultrasonic treatment to attain complete de-aggregation prior to analysis. By using the five different kaolinites, roughly the shortest and longest times needed for both soaking and ultrasonic treatment could therefore be obtained for kaolinites in general (sections 4.1.3.1 and 4.1.3.2). The outcome on accuracy and reproducibility of intentionally varying both soaking and ultrasonic times could hence also be established.

Lastly, the testing of five dissimilar kaolinites could also reveal other effects on accuracy and reproducibility connected to kaolinite type, which was not thought of beforehand.

2.2 OTHER CLAY SPECIES FOR THE PREPARATION OF CLAY MIXTURES

Due to the many factors that can have an impact on the accuracy of the sedimentary particle size analysis of mixtures of various clays types, it was decided to examine different self-prepared clay mixtures (sections 5.2). Mixtures were made up of the three clay mineral types most abundantly present in soils *viz.* kaolinite, illite and montmorillonite.

Montmorillonite was taken as the representative for all swell-clays (smectites and mixed-layer clays). It has the largest, and most varying increase in particle size under different chemical and physical conditions (sections 1.5.8). Montmorillonite furthermore has the largest amount of particles below 0.56 μm, that would cause the most comprehensive Brownian diffusion of all swell-clays. For all of these reasons montmorillonite will affect the accuracy of clay mixtures the most of all swell-clay types. Illite has the highest surface charge, which, of all clay types, would most easily cause flocculation.

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[10] *"dry strength" refers to the breaking strength of clay after all pore and adsorbed water was removed by drying in an oven (Grim, 1962).*

To investigate the magnitude of inaccuracy during the particle size analysis of clay mixtures, a simple approach was followed: first, a particle size analysis was conducted separately for each of the clay mineral species. Thereupon, the three different clay types were mixed together in a series of samples, containing several unlike clay ratios. In conclusion, the analysis results of each clay mixture were compared with its theoretical particle size distribution. The latter was calculated by the compilation of the single particle size distributions of the three clay species at the same clay ratios as the actual clay mixtures.

The kaolinite used in all of these mixtures was Serina filler. It has the smallest fraction below 2 µm of all the kaolinite types. Its steep particle size distribution would therefore display the most detectable deviation for a small change in the single parameter under investigation. In contrast, Serina coater and Amazone coater are centrifuged during beneficiation to 78% < 2 µm and 99% < 2 µm, respectively. On this account both kaolinites have flat particle size distributions, which would both be insensitive to the intentional variation of a chosen parameter. Being stripped of their smallest particles, neither of them is representative of natural kaolinites either. Hence, by not using the centrifuged kaolinites when preparing clay mixtures insured that the largest part of the below 2 µm fraction was represented by the montmorillonite component – as would be the case in nature. This would most plainly display the influence of the presence of montmorillonite on accuracy and reproducibility of clay mixtures containing it.

The illite sample, used as the third component in clay mixtures, is a weathered tuff bed from in the Collingham Formation, Ecca Group, Karoo Basin of South Africa. It was sampled as semi-weathered rock in the Ecca Pass between Grahamstown and Fort Beaufort. Microscopic and X-Ray Diffraction analysis disclosed illite as the only mineral component (sample Ecc 14; Viljoen, 1995).

The third component of the clay mixtures, montmorillonite, was acquired from G&W Base & Industrial Minerals, Wadeville, South Africa. This clay is marketed as Ocean Bentonite MD, Blaauboschpoort type[11]. It is mined in weathered Ecca Group rocks on the farm Oceaan 64 (*sic.*), Koppies district, Orange Free State, and is also situated in the Ecca Series. According to Schmidt (1976) the presence of cristobalite indicates that this bentonite is probably an *in situ* alteration product of volcanic ash. It is considered as an exceptionally pure montmorillonite, very similar to the so-called Southern Bentonites in the USA. The Oceaan Bentonite MD product datasheet states it has a montmorillonite content of typically 90 – 95%,

[11] *See G&W Base & Industrial Minerals website: www.gwbase.co.za*

containing small amounts of quartz, mica, and kaolinite.

In its natural state this montmorillonite has the exchangeable cations Ca^{2+} and Mg^{2+} in equal proportions (Schmidt, 1976). However, immediately after mining, it has a ± 30% water content. In this state it is immediately mixed with Na_2CO_3, to produce the Na^+ form through cation exchange (Roodt, 1998). Ocean Bentonite MD is specifically prepared in this manner for use as a drilling mud, as well as for the waterproofing of earthen dam walls.

3. THE APPARATUS-RELATED PARAMETERS

Accuracy is the measure of how close a measurement is to the true value. *Reproducibility*, in turn, is a measure of how close the results of multiple analyses, of *different samples* of the same material, are to each other. *Repeatability* (or precision), again, is a measure of how close the results of the repeated analysis of the *same sample* are to each other. Therefore when investigating any sample-related parameter, the experiments were designed in such a way that both the maximum extent of its effect, as well as the magnitude of the variation of its effect could be discovered. This would simultaneously give the magnitude of its effect on *accuracy*, as well as the magnitude of its effect on *reproducibility* and *repeatability*. This was achieved by keeping constant all known parameters that can have an effect, while varying one of them at a time.

To stop any apparatus-related parameters from interfering with the true effect of the single sample-related parameter under investigation, all of the former needed to be known in advance. Hence, before commencing with this study, all conceivable apparatus-related parameters of the Sedigraph 5000D were identified first. While all others parameters were kept constant, each one of the potential apparatus-related parameters was then tested separately, to determine the magnitude of its effect on accuracy and reproducibility.

Thereafter, whilst testing each sample-related parameter separately, all known apparatus-related parameters were kept constant, and at their levels favouring the highest degree of accuracy and reproducibility. When, during subsequent testing of a single parameter, a yet unidentified parameter (apparatus-related, or any other) was discovered for the first time, the experiments affected by it were repeated.

The following precautions were developed to maintain the apparatus-related parameters as constant as possible:

- A sheet of graph paper was covered by clear adhesive plastic, and permanently fixed in the same place on the recorder. During the course of each analysis, values of interest were read off the fixed graph paper, and recorded. Afterwards the graph's pen-trace was erased in preparation for the recording of the next analysis. This method assured the elimination of data fluctuations from one analysis to the next due to differences in printing and dimensions between different sheets of

graph paper, and due to potential differences in its placing on the recorder. This also saved on the time needed to fit new graph paper between analyses.

- The electronic safety switch for cutting power to the X-ray tube was by-passed. It switches off the X-ray tube when the door is opened to wash and fill the cell, and to fit tube clamps just before the start of an analysis. Bypassing the cut-out switch eliminated the temporary increase in X-ray intensity that affects the accuracy of the ensuing analyses.

  The likely diversity in duration of these interruptions would also produce variations in the recovery of X-ray intensities, and as a result also compromise the reproducibility. However, with the cut-out switch by-passed, the detector was exposed to sudden spikes in high X-ray intensity when the cell was removed for filling and washing. To protect the detector, a lead plate was installed that automatically lowered to cut off the X-rays when the door was opened.

- All temperature readings – needed for accurate cell scan rate calculations – were conducted by a thermocouple attached to its bottom. It was used instead of the Sedigraph's own mercury thermometer. The latter is inaccurately placed on the sample compartment wall – far enough away from the sample cell to lead to inaccurate results.

- The sample cell temperature was continually monitored during the full course of each analysis. With every 0.1 °C rise in cell temperature during the analysis, the cell scan rate was adjusted to safeguard accuracy.

- The clay suspensions, as well as the distilled water used to wash the cell after each analysis and to adjust the 0% setting, were always heated to 1.5 °C above the cell temperature recorded at the end of the previous analysis. This was conducted on a heating plate fitted with a magnetic stirrer. Heating of water and suspensions was to compensate for the loss of cell temperature to cooler air entering the cell compartment during washing and filling of the cell. This minimised temperature rise during the succeeding analysis, and hence reduced potential turbulence generated by temperature convection in the sample cell. This in turn improved accuracy, reproducibility, and repeatability.

- To obtain more accurate and reproducible cmp values, they were always read off the graph at the average value of electronic noise with a plastic strip. This was

carried out to the nearest 0.5 of a percent. To further reduce the undesirable result of electronic noise, the average of the trace of the recorder pen on the graph paper was used to more accurately adjust the 0% and 100% settings before the start of each analysis. Both these measures were to reduce the effects of electronic noise, and improved accuracy and reproducible.

- After each analysis the tip of the sample cell's suction pipe was washed with a water bottle. Only then it was lowered into the 100 ml container to pump heated wash water through the cell. The reason is that the same water is also used to fill the cell in preparation of the 0% setting. Otherwise clay suspension remained in the first 5mm of the suction pipe, gradually contaminating the wash water. This leads to wrong 0% settings, resulting in an unobserved and gradual lowering of cmp values. The same happens with the tip of the thermocouple, since it is used to monitor temperature during the warming of both the sample suspension and the wash water. Hence, likewise, the tip of the thermocouple was also washed after monitoring suspension temperatures.

Before commencing to test the effects of these apparatus parameters, though, all variations in sample parameters that could mask the effect of the single parameter under investigation also had to be eliminated.

The following precautions were taken to maintain the sample parameters as constant as possible:

- Kaolinites were used, due to the already mentioned reasons: it is mono-mineralic, offers a wide choice, is virtually homogeneous, has a small variation in density, is easy to disperse, and has the correct particle size range for sedimentary particle size methods (section2.1).
- The bulk samples were carefully ground with mortar and pestle to avoid size reduction of individual clay particles (see section 4.1.3.1 for the potential magnitude of its effect).
- After that, to further improve reproducibility: the bulk samples were homogenised by simultaneously shaking and rotating them for 1 min. in an irregular fashion in a closed container. This was to prevent the separation by gravity of smaller and larger agglomerates, with the smaller particles below and the larger ones above. This would have happen if the container remained in an upright orientation during

shaking. Clear evidence of the latter is seen while samples are being sieved on a sieve-shaker. After homogenisation, the bulk samples were divided into smaller samples by means of a spinning riffler.

- After distilled water plus deflocculant were added to the dry clay, the final steps to secure reproducibility were:
    - o shake all clay suspensions for a same duration (10 sec.),
    - o then sonicate each one for equal 3 min. periods in the same ultrasonic bath (section 4.1.3.1),
    - o and lastly, to re-suspend the larger particles that had deposited at the bottom during sonication, all samples were shaken again for equal periods of 10 sec.

In addition to the above, the *experimental conditions* (temperature, and concentrations of dispersants and suspensions) were kept as constant as possible.

Since all the above measures were strictly observed during all analyses, it will henceforth not be mentioned again in the descriptions of experimental procedures – accept where deemed appropriate.

3.1 PARAMETERS ASSOCIATED WITH INSTRUCTION MANUAL PROCEDURES

The first apparatus-related parameters to be investigated for its potential impact on accuracy and reproducibility were those associated with procedures prescribed in the Sedigraph 5000D instruction manual. They are the following:

- the result if pipe clamps are not used during analysis,
- the result if the magnetic stirrer is not used during 100% adjustments
- the effect if X-ray tube warm-up is ignored
- potential plotter drift if apparatus warm-up is ignored
- the consequence of electronic noise when the instruction manual method of "tapping" of the pen is used during adjustment of the 0% and 100% settings directly preceding each analysis,
- the effect of electronic noise when guessing the cmp values from the undulating plotter graph,

- and the result of using incorrect temperature measurements obtained by the inappropriately placed Sedigraph mercury thermometer

Preliminary tests investigating the first four procedures above revealed that using them had no negative impact. In fact, should they be ignored: accuracy and reproducibility would not noticeably be reduced. However, upon testing the last three prescribed procedures it was found that they did act negatively on accuracy and reproducibility. For this reason the substitutive procedures for the Sedigraph 5000D, already described above, were developed to keep these parameters in check.

The instrument design of the latest model, Sedigraph 5100, in the meantime eliminated the possibility of the above-mentioned apparatus-related parameters to have an influence on accuracy and reproducibility. It is first of all computer controlled, and fully automatic: it can successively load and analyse up to 18 samples. Its mixing chambers are situated outside the instrument, and the sample is automatically pumped to the sample cell situated inside the instrument. As a consequence, the need to switch off the X-rays at any time between successive analyses is done away with, along with the possible error caused by it. It washes the sample cell after each analysis, and thereafter automatically adjusts the 0% and 100% settings.

The controlling PC furthermore supplies its data in table or graph-form. Hence the need for manually reading off the graph with a plastic strip, in order to obtain accurate data, is averted. In this way all possible negative effects of electronic noise were removed.

The new instrument also has automatic temperature control, with heaters situated in the mixing chamber. Hence the dangers to inaccuracy and reproducibility related to both temperature convection and inaccurate temperature measurement are eliminated. Due to its automatic sample-loading set-up the need for pipe clamps, and the manual operation of a magnetic stirrer, are also eliminated.

After the samples are manually loaded, and the apparatus is switched on, it automatically warms the X-ray tube before starting with the first analysis. Therefore, the danger to accuracy and reproducibility if the mandatory warm-up period is forgotten was also removed.

The X-ray tube of the older model Sedigraph 5000D has a limited lifespan of about 15 to 20 years. However, the manufacture of its X-ray tubes has already been terminated a few years ago. Hence, within the next five to ten years, the abovementioned measures to keep the apparatus parameters of the Sedigraph 5000D at an optimum will be obsolete. It was therefore

decided not to submit the tests of the apparatus-related parameters as part of this thesis. However, the descriptions, conclusions, and data of all experiments to test the apparatus-related parameters are available on CD disk on the back page of this book (ApparatusParameters.doc), along with a soft copy of this thesis (Tesis2.doc).

4. TESTING THE EFFECT OF SAMPLE-RELATED PARAMETERS ON ACCURACY AND REPRODUCIBILITY

The sample-related parameters can be sub-divided into those relating to sample preparation, and those relating to the physical and chemical properties of the suspension.

The sample preparation procedures are those steps taken to obtain a small sample for analysis that is representative of the whole, and which is adequately dispersed to ensure accurate analysis of single particles. Omitting any of them, or conducting them improperly, will reduce accuracy, reproducibility, and repeatability of the analyses results.

The parameters related to the physical and chemical properties of the suspension include: the modification of the density and viscosity of the suspension liquid by the deflocculant, the influence of a high solid concentration, and hydrolysis due to the chemically active clay surfaces. If these factors are not sufficiently compensated for, then the accuracy of the analysis results will suffer.

Experiments investigating the impact on accuracy, reproducibility and repeatability of each of these parameters are discussed below.

4.1 POTENTIAL NEGATIVE EFFECT OF IMPROPER SAMPLE PREPARATION METHODS

The sample preparation procedures for particle size analysis are (Jackson, 1968; Gee and Bauder, 1986; Allen, 1995):

- de-aggregation by chemical dissolution
- size fractionation and sample-splitting
- removal of soluble salts by washing with polar organic solvents or heated water
- drying and grinding by mortar and pestle
- homogenisation and deflocculation
- ultrasonic treatment

Tests to determine the magnitude of the effects on accuracy and reproducibility when the last four parameters are done incorrectly will be discussed next. The potential detrimental

effects of omitting de-aggregation by means of chemical dissolution, or over-treatment with it, were already discussed in section 1.5.7.2. The potential impact on accuracy and reproducibility of size fractionation and sample-splitting was not investigated. When deemed necessary, though, both these techniques were used, and are mentioned in the relevant experimental procedures.

4.1.1 Inaccuracy due to the presence of soluble Salts

The ions of dissolved soluble salts depress the double layer, and enhance flocculation (section 1.5.5.1.2). However, when a deflocculant is added, the net (–) charge on all clay particle surfaces increases, which widens the double layer right round it (section 1.5.5.2). Thus, the flocculation effect of dissolved salts is counter-balanced, which is called peptization antagonism (van Olphen, 1977). The general belief therefore is that when adding a deflocculant to natural clays, the flocculation effect of the small amounts of soluble salts always present in natural clays will be completely defeated.

What must be kept in mind, though, is that even though the double layer is wider after adding a deflocculant, it will still be depressed by the presence of an electrolyte. Research also showed that when salt is added, the loops and tails of the deflocculant polymers, that is beneficial to deflocculation, disappear (section 1.5.5.2). Hence, both these effects accompanying dissolved salts should decrease the deflocculating capability of deflocculants.

It was therefore necessary to investigate whether the small amount of soluble salts occurring in natural clays would noticeably affect accuracy – even when dispersed with a deflocculant at optimum concentration.

Materials and methods:

To achieve the above objective, the particle size distribution of an unwashed Serina filler 1 sample was compared to that of the Serina filler 1 sample that had been washed centrifugally with distilled water (Table 4.1.1.1). Both samples were made up at the same solid concentration, and deflocculated at the same 1.0% Dispex concentration.

To calculate the error due to possible presence of soluble salts in the natural kaolinite sample the cmp values of the unwashed sample were subtracted from the water-washed one (Table 4.1.1.1). The pH of both samples was also determined just prior to particle size analysis. This was to establish whether a possible difference in pH could have improved the deflocculation of any of the samples, and thus have compromised the observation of the effect

of soluble salts (section 4.1.2.2).

Table 4.1.1.1. Testing the effect of soluble salts on the accuracy of kaolinite particle size analysis

Deflocculated with 1.0% Dispex

EQ. SPH. DIA. (μm)	CUMULATIVE MASS PERCENTAGE			
	Serina filler 1			Serina filler 2 Unwashed (Beneficiated with recycled water)
	Unwashed pH = 6.92	Water-washed pH = 7.13	Error due to presence of soluble salts	
1		45.3		
2	55.4	60.0	-4.6	60.4
3	65.1	70.1	-5.0	70.3
4	72.3	77.2	-4.9	77.3
5	77.4	83.0	-5.6	82.3
6	81.9	86.9	-5.0	86.1
8	88.2	92.3	-4.1	91.3
10	92.4	95.2	-2.8	94.4
20	100	100.0	0.0	99.5
30	100	100.0	0.0	100.3

Results and Discussion:

The water-washed sample gave noticeably higher cmps in the smaller and middle particle sizes; the difference was as high as 5.6% cmp.

Centrifugal washing slightly changed the pH from 6.92 in the unwashed sample to pH 7.13 in the washed sample – which is slightly above the p.z.c. at the edges in distilled water. But this, though, could not have made a great difference. When deflocculated with Dispex, the change in cmp below 2 μm caused by the rise in pH from acidic to just above neutral is only in the order of 0.8% (see Table 4.1.2.2.1 (b)). Therefore the major contribution to the above-mentioned difference of 5.6% cmp between the unwashed and washed samples was owing to the presence of soluble salts.

Further proof of the effect of soluble salts is detected when comparing the particle size analysis results of this water-washed Serina filler 1 sample, with that of an unwashed Serina filler 2 sample (Table 4.1.1.1). Serina filler 2 has the same mineral content as Serina filler 1, but is beneficiated in recycled water. Serina filler 2 therefore has a slightly higher salt content than Serina filler 1. As a consequence the cmp values differ from each other despite the

presence of a deflocculant. However, when the Serina filler 1 sample is centrifugally washed to remove its soluble salts, it exhibits more or less the same particle size distribution as that of Serina filler 2

Conclusions:

1) In all cases where the sizes of *single particles* of the essence during particle size analysis, then as a standard procedure all clay samples must beforehand be washed centrifugally with water, or dialyzed to remove all soluble salts. This will improve the *accuracy* of the results. Should all samples then also be dispersed with the same dispersant, and the pH adjusted to the same value of 9.5, then the results will be repeatable and reproducible in terms of all major chemical parameters.

2) Most soils are pre-treated with chemical dissolution methods, and then centrifugally washed afterwards to remove all chemicals used for it. There can, however, be a substantial difference of as large as 5.6% cmp between washed and unwashed samples. Hence samples that are centrifugally washed cannot be compared with samples that are unwashed – even in the presence of a deflocculant. Therefore to insure comparability of results between samples with, and without dissolution pre-treatment, it would be best that prior centrifugal washing is included in a standard procedure, even for particle size analysis of single clays.

3) Tables 4.1.2.1.2 (a) to (e) illustrate that the removal of soluble salt is not essential to assure good *repeatability* when using a deflocculant: The standard deviations of all kaolinite types indicate that repeatability remained excellent, despite the presence of small amounts of soluble salts.

   Hence, the soluble salts can safely remain in clay samples when only comparability is at stake. Accordingly, to save time during this study, soluble salts were not removed beforehand when the effects on accuracy and reproducibility of the other parameters were investigated.

4.1.1.1 Inaccuracy when organic polar liquids are used during centrifugal washing

The standard procedures for centrifugal washing normally prescribe the use of polar organic liquids such as ethanol, methanol, and acetone (Jackson, 1968; Klute, 1986). They are used to both remove soluble salts, and to simultaneously cause flocculation to facilitate fast retrieval of samples during centrifugation.

However, a test conducted on a kaolinite suspension showed that after centrifugal washing

with methanol, some stayed behind in the wet sediment. Drying and weighing the sediment, showed that approximately 1 gram of methanol was retained for each gram of dry clay.

The sediments were then re-suspended with 100 ml of water, and heated in a water bath at 80 °C in an attempt to evaporate the methanol (the boiling point of methanol is 68 °C). When after 1½ hour of evaporation the hot suspensions were not disturbed, there was no smell of methanol. Yet, each time the sediment was re-suspended by stirring, a clear smell of methanol re-appeared.

Since ethanol, methanol, and acetone are flocculating agents, the question was: if some of them remained behind after the centrifugal washing to remove soluble salts, would it compromise accuracy during subsequent particle size analysis? To test this, the following experiment was conducted on a kaolinite sample.

Materials and Methods:

Four Serina filler 1 samples were made up at 3.85% solids by volume. One of them was given two centrifugal washings with ethanol; the second one, two washings with methanol; and the last one the same with acetone. The first washing was with a 50:50 mixture of distilled water and organic polar liquid, and a second one with organic polar liquid only. After washing was completed, the clay deposited at the bottoms of the centrifuge tubes were re-suspended with distilled water, and the polar liquid sample was evaporated in a water bath for 1 hour. A temperature of just over 85 °C was reached, which is above the boiling points of all three polar liquids (ethanol 78.2 °C, methanol 64.6 °C, and acetone 56.05 °C) (Linde, 2002).

The fourth sample was centrifugally washed with distilled water, to obtain a standard against which to test the effect of the three polar liquids on accuracy. However, repeated centrifugal washing of a clay suspension in cold water desalinates it. This leads to deflocculation, and therefore prevents complete centrifugal recovery. The result is a particle size distribution differing from the organic liquid samples, thus compromising the use of the water-washed sample as a standard. Therefore, the latter was pre-heated to 80 °C in a water-bath to induce flocculation. The second washings of all samples showed no trace of chlorides when tested with 0.1M $AgNO_3$.

Afterwards, while being weighed, all samples were made up to the appropriate solid concentration by adding the correct amounts of distilled water and 6 g/l Dispex stock solution to obtain a 3.85 % solid concentration at a 1.0% Dispex concentration. To acquire the accurate solid concentration, the mass of polar liquid remaining in the sample after centrifugal washing

had to be compensated for. To achieve this, the dry centrifugal tube was weighed first, before the samples of known mass were added to it. After washing, the appropriate amount of Dispex stock solution was added. Finally, the centrifuge tube was placed on a scale, and distilled water was added until it reached the following tube mass:

$$Tube\ mass = 4.5g\ Clay + 31.25g\ (polar\ liquid + water) + 11.25g\ Dispex + Mass\ empty\ tube$$

A second way of getting rid of the polar liquids before particle size analysis was to evaporate them in an oven. Therefore, three further Serina filler 1 samples were centrifugally washed with the same organic polar liquids, but thereafter were dried overnight in an oven at 95 °C. The dried samples were removed as quantitatively as possible to a mortar. After being ground, they were re-combined to their respective centrifuge tubes. The appropriate amounts of distilled water and Dispex stock solution were added, and the tubes were shaken to remove the last traces of sample still sticking to the bottoms of the tubes. All of the largest particles were thus retrieved, ensuring an accurate standard against which to test the evaporated samples.

However, the centrifugal washing with different organic polar liquids could have resulted in suspension pH values different from that of the water-washed sample. Since their potential differences in pH could have affected analyses results, it could have masked the real effects of the organic polar liquids when comparing them with the water-washed sample. Hence, the pH of all samples was adjusted to 9.5 with Na_2CO_3. Thereafter a 3 min. ultrasonic treatment was given for each, and their size analyses conducted immediately afterwards.

All the analysis results of the water-washed and polar liquid washed samples (evaporated or oven-dried), and the differences in cmp between them, are given in Table 4.1.1.1.

Result and Discussion:

The ethanol samples evaporated in a water bath clearly had some degree of flocculation despite the use of Dispex. The smaller particle sizes had smaller cmp values than the water washed sample, whereas the larger particle sizes had larger cmp values. This should be due to some ethanol remaining even after evaporation for 1 hr., or can be ascribed to impurities in the laboratory grade methanol used during the centrifugal washing. With the methanol and acetone samples, flocculation increased as particle size decreased.

Table 4.1.1.1. The differences of the effect of centrifugal washing with ethanol, methanol, and acetone on the cmp values of kaolinite

All samples deflocculated with 1.0% Dispex at pH 9.5

EQ. SPH. DIA. (μm)	CUMULATIVE MASS PERCENTAGE				
	WATER-WASHED	ETHANOL-WASHED			
		Evaporated in water bath 1.5 hr.		Evaporated in oven overnight	
	Initial pH = 7.43 Adjusted pH = 9.5	Initial pH = 7.55 Adjusted pH = 9.51	**Error due to presence of Ethanol**	Initial pH = 7.40 Adjusted pH = 9.50	**Difference with water-washed sample**
1	47.4	44.3	-3.1	47.0	-0.4
2	60.4	59.0	-1.4	60.9	0.5
3	70.6	70.1	-0.5	71.2	0.6
4	77.1	77.4	0.3	78.0	0.9
5	82.0	82.1	0.1	82.4	0.4
6	85.9	86.3	0.4	86.0	0.1
8	91.0	92.1	1.1	91.4	0.4
10	94.3	95.6	1.3	94.3	0.0
20	100.0	99.9	-0.1	99.9	-0.1
30	100.0	100.0	0.0	100.0	0.0

EQ. SPH. DIA. (μm)	CUMULATIVE MASS PERCENTAGE				
	WATER-WASHED	METHANOL-WASHED			
		Evaporated in water bath 1.5 hr.		Evaporated in oven overnight	
	Initial pH = 7.43 Adjusted pH = 9.5	Initial pH = 7.55 Adjusted pH = 9.51	**Error due to presence of Methanol**	Initial pH = 7.37 Adjusted pH = 9.51	**Difference with water-washed sample**
1	47.4	44.9	-2.5	47.0	-0.4
2	60.4	57.8	-2.6	61.1	0.7
3	70.6	69.0	-1.6	71.1	0.5
4	77.1	76.2	-0.9	77.9	0.8
5	82.0	81.2	-0.8	82.5	0.5
6	85.9	85.5	-0.4	86.4	0.5
8	91.0	91.1	0.1	91.2	0.2
10	94.3	94.2	-0.1	94.2	-0.1
20	100.0	100.0	0.0	100.0	0.0
30	100.0	100.0	0.0	100.0	0.0

Table 4.1.1.1. Continued

EQ. SPH. DIA. (μm)	CUMULATIVE MASS PERCENTAGE				
	WATER-WASHED	ACETONE-WASHED			
		Evaporated in water bath 1.5 hr.		Evaporated in oven overnight	
	Initial pH = 7.43 Adjusted pH = 9.5	Initial pH = 7.48 Adjusted pH = 9.52	**Error due to presence of Acetone**	Initial pH = 7.37 Adjusted pH = 9.51	**Difference with water-washed sample**
1	47.4	45.1	-2.3	47.8	0.4
2	60.4	55.8	-4.6	61.9	1.5
3	70.6	68.4	-2.2	72.3	1.7
4	77.1	75.9	-1.2	79.1	2.0
5	82.0	81.0	-1.0	84.0	2.0
6	85.9	85.1	-0.8	87.3	1.4
8	91.0	90.5	-0.5	92.1	1.1
10	94.3	94.2	-0.1	95.1	0.8
20	100.0	99.9	-0.1	100.0	0.0
30	100.0	100.0	0.0	100.0	0.0

The general pattern of all samples shows that as the ability of the organic dipole to flocculate clay suspensions increases, the size of the errors increases, and the larger the particle sizes became that are affected. Cmp differences between –3.1% and 1.3% cmp were recorded for the ethanol washed sample, between –2.6% and 0.1% cmp for the methanol washed sample, and between –4.6 and 0.0% cmp for the acetone sample.

Surprisingly, when the ethanol and methanol were evaporated in an oven overnight, all the samples apparently gave slightly better dispersion than the water-washed sample. With the acetone sample, improvement of up to 2.2% is observed. One explanation can be found in the fact that the organic solvent samples were re-ground after being dried, whereas the water-washed sample was re-suspended for particle size analysis directly after washing. Re-grinding could have decreased the particle size of the organic solvent samples.

These samples, however, needed only light grinding to pulverise them. A more likely explanation therefore is that a small amount of organic solvent molecules remained on the clay surfaces that improved stability. The same was reported by Rengasamy (1982) for Ca-montmorillonite after an ethanol treated sample was dried, reground, and re-suspended (section 1.5.7.1).

Conclusions:

1) Since re-grinding could have increased the smaller particle sizes, the answer to the question whether samples desalinated with organic solvents can be oven-dried, must be viewed as inconclusive. Therefore, for the time being, centrifugal washing with distilled water is viewed as the safest option for fast desalination.

2) During centrifugal washing with distilled water, flocculation can be accomplished by firstly heating the sample suspensions in a water-bath to at least 80 °C, just before each centrifugal washing. Secondly, centrifugation should be conducted for 10 – 15 min. at 3000 r.p.m. When the smallest particles of some samples thereafter still remain suspended (notably Na-montmorillonite), the pH of only the supernatant must be adjusting to 5.0 with a few drops of 0.001M HCl. Shaking to re-suspend the tightly packed sediments after such high r.p.m is very time consuming (up to ½ hr. and more). However, using a ball-shaped rubber plunger to the design of Jackson (1968), facilitates re-suspension within only 10 – 15 sek.

Suggestions for further study:

The above experiment must be repeated, but also oven-dry an additional water-washed sample along with those of the organic dipole samples. Do the same experiment with montmorillonite and illite to investigate to what extend the same conditions will influence the particle size analysis of these clays.

4.1.2 Influence of deflocculation procedures on accuracy and reproducibility

When adding just enough deflocculant, an unstable suspension abruptly changes to a stable one. The question, however, is whether deflocculation is complete; *i.e.* does an unstable suspension immediately change to completely separate single particles? At the minimum amount of deflocculant to secure a stable suspension, does it still retain some flocks? Would the sizes of the remaining flocks be reduced if more dispersant is added? How much can accuracy and reproducibility be affected when deflocculation is conducted improperly.

Furthermore, own experience during viscosity measurements on thick clay suspensions (60% by weight) had demonstrated when adding deflocculant at an optimum concentration, a minimum viscosity was reached. But further addition of deflocculant again increased the viscosity of high solids slurries. Over-dispersing therefore reduces the stability of thick clay suspensions. Would this also happen at the very low solid concentration of ± 9.0% by weight used for Sedigraph analyses? On this account the aim of the experiment, described in the next

section was to develop a procedure to determine optimum deflocculant concentration of a clay suspension during Sedigraph analysis. Thereafter, further improvement in stability is demonstrated when Na_2CO_3 is used, in conjunction with a deflocculant. Na_2CO_3 is utilised to increase the pH high enough above that of the p.z.c. at the edges to add to the total negative all round surface charge.

4.1.2.1 Obtaining the optimum deflocculant concentration

The optimum amount of deflocculant is determined firstly by the total amount of positive (+) edge-charge (van Olphen, 1977). The finer a kaolinite, the larger its total surface area, hence the higher will be the total (+) surface charge. As a consequence, the finer a kaolinite, the more deflocculant it needs for optimum dispersion (Angel and Vincent, 1978).

Secondly, with some kaolinites a very thin layer of amorphous coating on their surfaces will also enlarge the (+) surface charge. This will likewise increase its optimum deflocculant concentration. The type and amount of amorphous surface coatings can differ from one clay to the next. This will widen the diversity in optimum dispersant concentrations between various kaolinites types.

For both the above reasons different clays need different amounts of deflocculants to achieve optimum dispersion when suspended in liquid. It was therefore necessary to determine the optimum deflocculant concentration for each of the kaolinite/deflocculant combinations right at the start of this study. This would secure optimum dispersion when later testing the other parameters. It would additionally indicate whether it is feasible to use one standard optimum deflocculant concentration that will suit all kaolinite types.

To achieve this, a series of samples with increasing deflocculant concentrations were analysed for each kaolinite/deflocculant combination. The deflocculant concentration of the first analysis in a series that reached the highest cmp values was viewed as the optimum deflocculant concentration.

Materials and Methods:

For optimum dispersion of clays very small concentrations of 1% or less (mass deflocculant as supplied/mass clay) are necessary. Therefore very small amounts of deflocculant are necessary to deflocculate the small samples used with Sedigraph analyses.

The four types of deflocculants used during this study are supplied as a dry powder, or in concentrated liquid form with syrup-like consistency. To prevent the time consuming

weighing of small amounts of deflocculant before every analysis, each deflocculant was first diluted into a stock solution with water. Bigger amounts of stock solution could now quickly and accurately enough be measured off with a blow-out pipette. Next distilled water was added to further dilute it to the required amount and concentration. Finally, the dry clay sample was added to make up the sample suspension.

The following equation was derived to calculate the amounts of stock solution plus water necessary to acquire several different deflocculant concentrations:

$$Deflocculant\ Conc. = \left[\frac{(V_{Stock.}) \times \frac{C_{Stock}}{1000}}{M_{Clay}} \right] \times \frac{100}{1} \qquad \text{Eq. 4.1.2.1.1}$$

with $V_{Stock.}$ the volume of stock solution, C_{Stock} the concentration of the deflocculant stock solution in g/l (mass deflocculant as supplied/litre water), and M_{Clay} is the mass of clay to be suspended in grams. In the above formula $V_{Stock.}$ is taken as equal to its mass, since the density of the suspension solution is very close to 1 g/cm^3.

Deflocculant concentrations calculated with Eq. 4.1.2.1.1 are for the specific mass of clay (M_{Clay}) necessary to attain the particular solids content needed for a Sedigraph analysis to be accurate. To get acceptable Sedigraph accuracy, the amount of X-rays transmitted through a mineral suspension must be within certain limits (section 4.2.2). The density of a particular mineral determines its X-ray absorbency. Accordingly the suspensions of different minerals will need distinct solid concentrations to transmit the same required amount of X-rays.

The correct solids content for kaolinite, specifically for the X-ray tube used during this study, was beforehand determined experimentally (section 4.2.2.1). A solids content of 9.52% by weight (3.85% by volume) was found to be appropriate to satisfy all instrumental demands.

In order to make up the required solid concentration, the total volume of liquid (V_l) to be added to a sample of chosen mass (M_{Clay}), must first be calculated. For this the following formula was derived:

$$Solids\ Concentration\ \left({}^{W}/_{W}\right) = \left(\frac{M_{Clay}}{M_{Clay} + V_l} \right) \times \frac{100}{1} \qquad \text{Eq. 4.1.2.1.2}$$

In the above equation the total mass of liquid (water plus stock solution) is once again used in place of V_l due to the closeness of its density to 1 g/cm^3.

Before doing the above calculation, an appropriate mass of clay had to be chosen. For the

Sedigraph 5000D sample set-up, samples of more or less 9 g were enough for easy filling, as well as for re-suspending deposited clay at the bottom of the cell through pumping after the completion of an analysis. Using Eq. 4.1.2.1.2, the total volume (V_l) to secure the required solid concentration of 9.52% by weight necessary for 9 g kaolinite samples, was calculated at 85 cm^3.

By then using Eq. 4.1.2.1.1, the V_{H_2O} and V_{Stock} for a number of different deflocculant concentrations were calculated for 9 g kaolinite samples in a total volume of liquid of $V_l = 85$ cm^3. The results are given in Table 4.1.2.1.1.

A 6 g/l stock solution was chosen from Table 4.1.2.1.1 to determine the optimum deflocculant concentration. It could supply dispersant concentrations of up to 5.5% before the concentration of the stock solution itself was reached (no series of analyses in this experiment were conducted deflocculant concentrations of over 5% (Tables 4.1.2.1.2 (a) – (d)). Furthermore, 6 g/l stock solutions required volumes that, with the specific inaccuracy of a blow-out pipette, would give solid concentrations that would still be accurate and repeatable enough.

The experimental procedure to secure the optimum dispersant concentrations for every kaolinite type was as follows:

Four different kaolinites were used *viz.* Dinkey filler, Serina filler 2, Dinkey coater and Amazone coater. These four kaolinites were chosen since between them they had a wide range in the amount of fine particles. This could, from one kaolinite to the next, exhibit the increase in the optimum deflocculant concentration that should accompany the enlargement in total surface area from one kaolinite type to the next. For each kaolinite/deflocculant combination a total of twenty 9 gram samples were weighed accurate to the third decimal from splitter samples.

By using Table 4.1.2.1.1, sample suspensions were prepared that ranged in deflocculant concentration from 0.1% - 5%. This was done with four different types of deflocculants *viz.* Calgon, Dispex, Floccotan, and TSP. The TSP deflocculant was acquired some time after the other three, at which time the Dinkey filler samples were already depleted. This explains the absence of test data for TSP deflocculant with Dinkey filler.

Table 4.1.2.1.1. Dilution of a number of stock solutions to obtain various deflocculant concentrations for Sedigraph particle size analysis.

The volumes of dispersant stock-solution and water are calculated to make up a 9.52% by weight (3.87% by volume) kaolin suspension as necessary for accurate Sedigraph analysis. The suspension consists of 9 g of kaolin in 85 cm3 of liquid (water + dispersant stock-sollution). The dispersant stock solution volumes are given for 5 different stock solutions concentrations.

DEFLOCCULANT CONCENTRATION	3 g/l Stock-solution.		6 g/l Stock-solution.		8 g/l Stock-solution.		10 g/l Stock-solution.	
(%)	VOLUME Stock Solution (cm^3)	VOLUME Water (cm^3)	VOLUME Stock Solution (cm^3)	VOLUME Water (cm^3)	VOLUME Stock Solution (cm^3)	VOLUME Water (cm^3)	VOLUME Stock Solution (cm^3)	VOLUME Water (cm^3)
0.1	3.00	82.00	1.50	83.50	1.13	83.88	0.90	84.10
0.2	6.00	79.00	3.00	82.00	2.25	82.75	1.80	83.20
0.3	9.00	76.00	4.50	80.50	3.38	81.63	2.70	82.30
0.4	12.00	73.00	6.00	79.00	4.50	80.50	3.60	81.40
0.5	15.00	70.00	7.50	77.50	5.63	79.38	4.50	80.50
0.6	18.00	67.00	9.00	76.00	6.75	78.25	5.40	79.60
0.7	21.00	64.00	10.50	74.50	7.88	77.13	6.30	78.70
0.8	24.00	61.00	12.00	73.00	9.00	76.00	7.20	77.80
0.9	27.00	58.00	13.50	71.50	10.13	74.88	8.10	76.90
1.0	30.00	55.00	15.00	70.00	11.25	73.75	9.00	76.00
1.1	33.00	52.00	16.50	68.50	12.38	72.63	9.90	75.10
1.2	36.00	49.00	18.00	67.00	13.50	71.50	10.80	74.20
1.3	39.00	46.00	19.50	65.50	14.63	70.38	11.70	73.30
1.4	42.00	43.00	21.00	64.00	15.75	69.25	12.60	72.40
1.5	45.00	40.00	22.50	62.50	16.88	68.13	13.50	71.50
1.6	48.00	37.00	24.00	61.00	18.00	67.00	14.40	70.60
1.7	51.00	34.00	25.50	59.50	19.13	65.88	15.30	69.70
1.8	54.00	31.00	27.00	58.00	20.25	64.75	16.20	68.80
1.9	57.00	28.00	28.50	56.50	21.38	63.63	17.10	67.90
2.0	60.00	25.00	30.00	55.00	22.50	62.50	18.00	67.00
2.1	63.00	22.00	31.50	53.50	23.63	61.38	18.90	66.10
2.2	66.00	19.00	33.00	52.00	24.75	60.25	19.80	65.20
2.3	69.00	16.00	34.50	50.50	25.88	59.13	20.70	64.30
2.4	72.00	13.00	36.00	49.00	27.00	58.00	21.60	63.40
2.5	75.00	10.00	37.50	47.50	28.13	56.88	22.50	62.50
2.6	78.00	7.00	39.00	46.00	29.25	55.75	23.40	61.60
2.7	81.00	4.00	40.50	44.50	30.38	54.63	24.30	60.70
2.8	84.00	1.00	42.00	43.00	31.50	53.50	25.20	59.80
2.9	*	*	43.50	41.50	32.63	52.38	26.10	58.90
3.0			45.00	40.00	33.75	51.25	27.00	58.00
3.5			52.50	32.50	39.38	45.63	31.50	53.50
4.0			60.00	25.00	45.00	40.00	36.00	49.00
4.1			61.50	23.50	46.13	38.88	36.90	48.10
4.2			63.00	22.00	47.25	37.75	37.80	47.20
4.3			64.50	20.50	48.38	36.63	38.70	46.30
4.4			66.00	19.00	49.50	35.50	39.60	45.40
4.5			67.50	17.50	50.63	34.38	40.50	44.50
5.0			75.00	10.00	56.25	28.75	45.00	40.00
5.5			82.50	2.50	61.88	23.13	49.50	35.50
6.0			*	*	67.50	17.50	54.00	31.00
8.0					*	*	72.00	13.00
10.0							*	*

* Larger dispersant concentrations are not possible at this stock solution, since the volume of dispersant that is needed would then be greater than the total volume of liquid (dispersant stock solution + distilled water = 85 cm^3) required for a 9.52% by weight solid content.

All kaolin types were given a 3 min. ultrasonic treatment in an ultrasonic bath just before every analysis. Very high deflocculant concentrations were needed to disperse Amazone, and the cmp values were very scattered (Table 4.1.2.1.2 (c)). In an attempt to rectify this the samples were soaked, in some cases re-sonicated, and analysed again. The need to soften

Amazone was confirmed by much harder aggregates being felt between fingertips after being ground, than the other kaolinite types.

Only the cmp values below 2 μm were recorded for each sample, since the smallest particle size presents the best indication as to how effective a clay was de-agglomerated: The better the de-agglomeration, the higher the cmp of the smallest particles. Since the smallest particles are the most likely to flocculate: the 2 μm particle size would also most clearly indicate the efficiency of each dispersant concentration.

The results for each kaolinite/deflocculant combination are presented in Tables 4.1.2.1.2 (a) – (d). Figures 4.1.2.1.1 (a) - (d) are used to give a visual representation of the usefulness of each deflocculant for each kaolinite type. The data when the 3 min. ultrasonic treatments were conducted directly after suspending the kaolinite were used to construct Figures 4.1.2.1.1 (a), (b) and (d) for the kaolinites Serina filler, Dinkey coater and Dinkey filler.

The optimum deflocculant concentrations (in bold) in Tables 4.1.2.1.2 (a) - (d) were transferred to Table 4.1.2.1.3, along with their corresponding cmp values. These results were plotted on Fig. 4.1.2.1.2 to easily compare the efficiency of the different deflocculants.

Results and Discussion:

Both Table 4.1.2.1.3 and Fig. 4.1.2.1.2 first of all verify that the finer the kaolinite, the more deflocculant is needed to attain deflocculation. The minimum deflocculant concentration needed to produce the first signs of stability ranged between 0.1% and 0.5%, depending on deflocculant type and the kaolinite type. A stable suspension can easily be identified on the Sedigraph plotter output. The graph exhibits undulations of only electronic noise proportions. It also shows a decrease in cmp values towards the smaller particle sizes, indicating an improvement in dispersion.

Secondly, Tables 4.1.2.1.2 (a) – (d) show that below these minimum deflocculant concentrations all the samples remained totally unstable. Signs of instability are clearly identifiable on the Sedigraph plotter output. Unstable suspensions form large flocks, which link together to form one single matrix (van Olphen, 1977). During the course of an analysis, the matrix compresses very slowly, but unevenly. Hence, the plotter graph exhibits large fluctuations in cmp, with its average staying just below the 100% cmp line right up to the smallest particle size. The graph of a stable suspension shows the opposite.

Table 4.1.2.1.2. Determination of optimum deflocculant concentrations for Serina, Dinkey and Amazone when using Calgon, Dispex and Floccotan as deflocculants.

(a) Serina filler 2

CALGON		DISPEX		FLOCCOTAN		TSP	
DISPERSANT CONC. (%)	Cmp < 2 µm Done immediately after 3 min. ultras.	DISPERSANT CONC. (%)	Cmp < 2 µm Done immediately after 3 min. ultras.	DISPERSANT CONC. (%)	Cmp < 2 µm Done immediately after 3 min. ultras.	DISPERSANT CONC. (%)	Cmp < 2 µm Done immediately after 3 min. ultras.
0.1	unstable	0.2	unstable	0.2	unstable	0.1	unstable
0.2	unstable	0.4	58.5	0.3	unstable	0.2	55.5
0.3	unstable	0.5	58.0	0.4	58.0	0.3	55.0
0.4	unstable	**0.6**	**59.0**	0.5	**58.0**	0.4	**56.0**
0.5	56.5	0.7	58.5	0.6	58.0	0.5	56.5
0.6	60.5	0.8	58.5	**0.7**	58.5	**0.6**	56.0
0.7	**59.5**	0.9	59.0	0.8	58.0	0.7	56.5
0.8	59.5	1.0	59.0	0.9	59.0	0.8	56.0
0.9	59.5	1.1	59.0	1.0	58.0	0.9	56.0
1.0	60.0	1.2	59.0	1.1	58.5	1	56.0
1.1	60.0	1.3	59.0	1.2	57.5	1.1	56.0
1.2	60.0	1.4	57.5	1.3	58.5	1.2	56.5
1.3	60.0	1.5	58.0	1.4	58.5	1.3	56.5
1.4	59.5	1.6	57.0	1.5	58.0	1.4	56.0
1.5	59.5	1.7	57.5	1.6	58.5	1.5	56.0
2.0	59.5	2.0	57.5	2.0	58.5	1.6	55.5
3.0	59.5	3.0	57.5	3.0	57.0	2.0	55.0
3.5	60.5	5.0	58.5	5.0	58.0	3.0	56.0
4.0	60.5					5.0	57.0
5.0	61.0						

Optimum deflocculant concentrations in bold

Fig. 4.1.2.1.1 (a). Serina filler 2

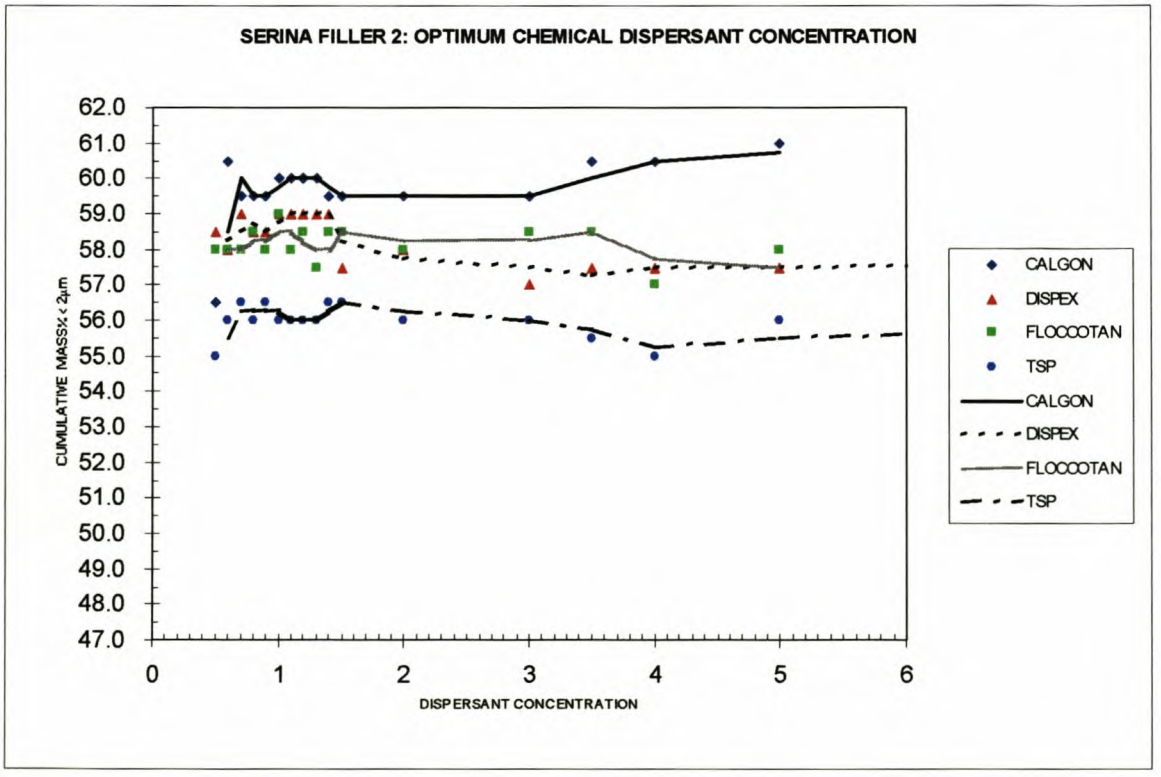


Table 4.1.2.1.2 (b). Dinkey coater (30 µm)

CALGON		DISPEX		FLOCCOTAN		TSP	
DISPERSANT CONC. (%)	Cmp < 2 µm Done immediately after 3 min. ultras.	DISPERSANT CONC. (%)	Cmp < 2 µm Done immediately after 3 min. ultras.	DISPERSANT CONC. (%)	Cmp < 2 µm Done immediately after 3 min. ultras.	DISPERSANT CONC. (%)	Cmp < 2 µm Done immediately after 3 min. ultras.
0.2	unstable	0.2	unstable	0.1	unstable	0.1	77.5
0.3	82.0	0.3	unstable	0.2	unstable	0.2	78.5
0.4	82.0	0.4	82.0	0.3	unstable	**0.3**	80.0
0.5	**82.5**	0.5	82.0	0.4	81.5	0.4	78.5
0.6	82.5	0.6	82.0	**0.5**	82.5	0.5	79.0
0.7	82.5	**0.7**	**82.5**	0.6	**82.0**	0.6	**79.0**
0.8	82.5	0.8	82.5	0.7	82.5	0.7	79.0
0.9	82.5	0.9	82.5	0.8	82.0	0.8	78.5
1.0	82.5	1.0	82.0	0.9	83.0	0.9	78.5
2.0	81.5	1.1	83.0	1.0	82.0	1.0	79.0
3.0	81.0	1.2	83.5	1.1	82.0	1.1	79.0
5.0	unstable	1.3	82.0	2.0	81.5	2.0	79.0
6.0	unstable	2.0	81.5	3.0	81.5	3.0	79.0
		3.0	82.0	5.0	82.5	5.0	79.5
		5.0	83.0				

Optimum deflocculant concentrations in bold

Fig. 4.1.2.1.1 (b). Dinkey coater (30 µm)

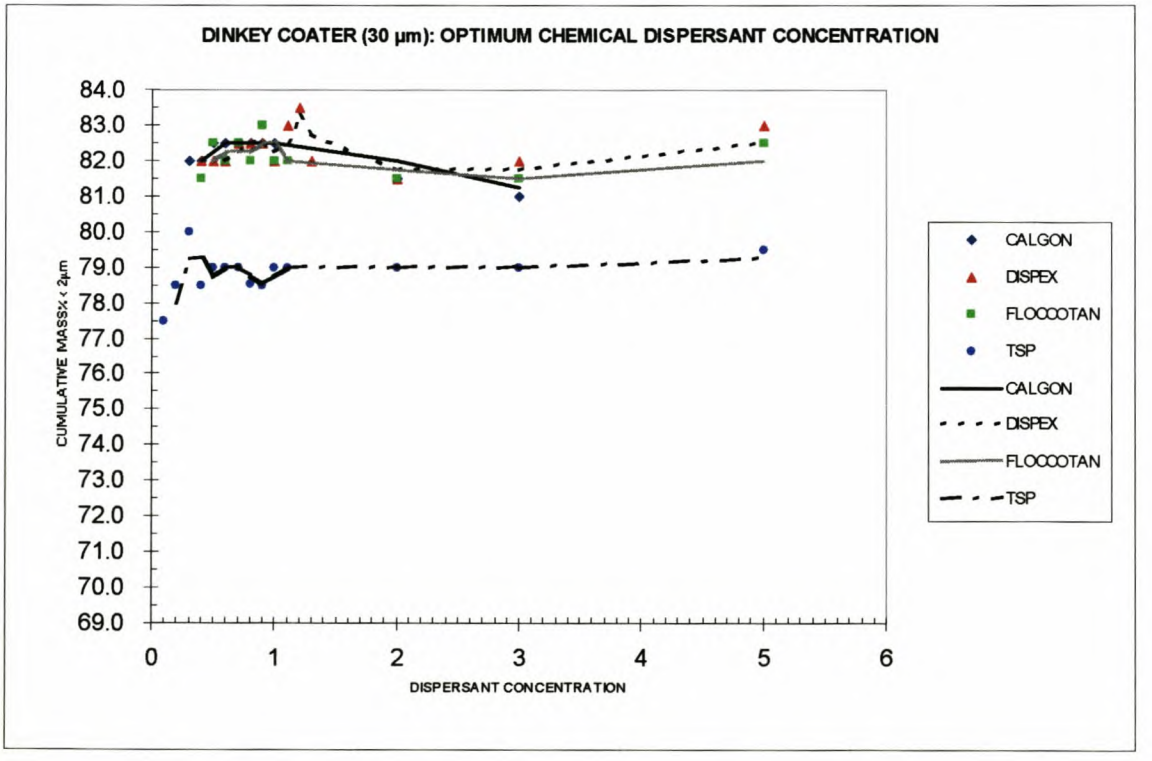


Table 4.1.2.1.2 (c). Amazone coater

Optimum deflocculant concentrations in bold.

DISPERSANT CONC.	CALGON Cmp < 2 µm		DISPERSANT CONC.	DISPEX Cmp < 2 µm			DISPERSANT CONC.	FLOCCOTAN Cmp < 2 µm		DISPERSANT CONC.	TSP Cmp < 2 µm
	SAME SAMPLE			SAME SAMPLE				NEW SAMPLE	NEW SAMPLE		
(%)	Done immediately, after 3 min. ultras.	Soaked for extra 5 days, extra 3 min. ultras.	(%)	Done immediately after 3 min. ultras.	Additional soaking for 3 days. Only 10 sek. shaking	Extra 3 min. ultras.	(%)	Soaked for **1** day Shake **10** sek. and then 3 min. ultras.	Soaked for **3** days. Shake **60** sek. and then 3 min. ultras.	(%)	SOAKED for 3 days, then 3 min. ultras.
			0.1	unstable	unstable	unstable	0.1	unstable	unstable	0.1	unstable
0.2	92.0	97.0	0.2	unstable	unstable	unstable	0.2	unstable	unstable	0.2	97.5
0.3	88.5	96.5	0.3	unstable	93.0	98.0	0.3	unstable	87.5	0.3	98.0
0.6	94.0	98.5	**0.4**	91.5	93.0	**99.0**	0.4	88.5	89.5	0.4	97.5
0.7	90.0	98.0	**0.5**	93.0	94.0	98.5	0.5	88.5	92.5	0.5	97.0
0.8	91.0	**99.0**	**0.6**	92.0	94.5	99.0	0.6	95.5	92.5	**0.6**	**98.5**
1.0	91.0	99.5	1.0	96.5	97.0	99.0	**0.7**	**96.5**	95.0	0.7	98.5
1.1	97.0	99.0	1.2	94.5	97.0	99.0	0.8	91.0	95.5	0.8	98.5
1.2	**97.5**	99.0	1.3	96.5	97.0	98.5	0.9	87.5	96.0	0.9	99.0
1.3	97.0	99.0	1.4	94.0	96.0	99.0	1.0	87.5	93.5	1.0	98.5
1.4	96.5	99.0	1.5	96.5	-	99.0	**1.1**	96.5	**97.0**	2.0	98.5
1.5	98.0	99.5	1.6	95.0	96.5	99.0	2.0	91.5	97.5	3.0	98.5
1.6	98.0	99.0	1.7	96.5	97.5	99.0	3.0	96.0	97.5	5.0	98.5
1.7	98.5	99.0	**1.8**	**99.0**	**99.0**	99.0	5.0	95.5	96.0		
1.8	97.0	99.0	1.9	97.0	Additional soaking 5 days.	99.0					
1.9	97.0	99.0	2.0	98.5	99.0	99.0					
2.0	96.5	99.0	2.1	98.5	99.0	99.0					
3.0	97.0	99.5	2.2	96.0	99.0	99.0					
5.0	97.0	99.0	2.3	95.0	97.5	99.0					
			2.4	94.5	98.0	99.0					
			2.5	98.5	98.0	99.0					
			3.0	97.0	99.0	99.5					
			5.0	96.0	97.0	99.0					
					99.0	99.0					

– : No particle size analysis done at the given dispersant concentration.

Fig. 4.1.2.1.1 (c). Amazone coater

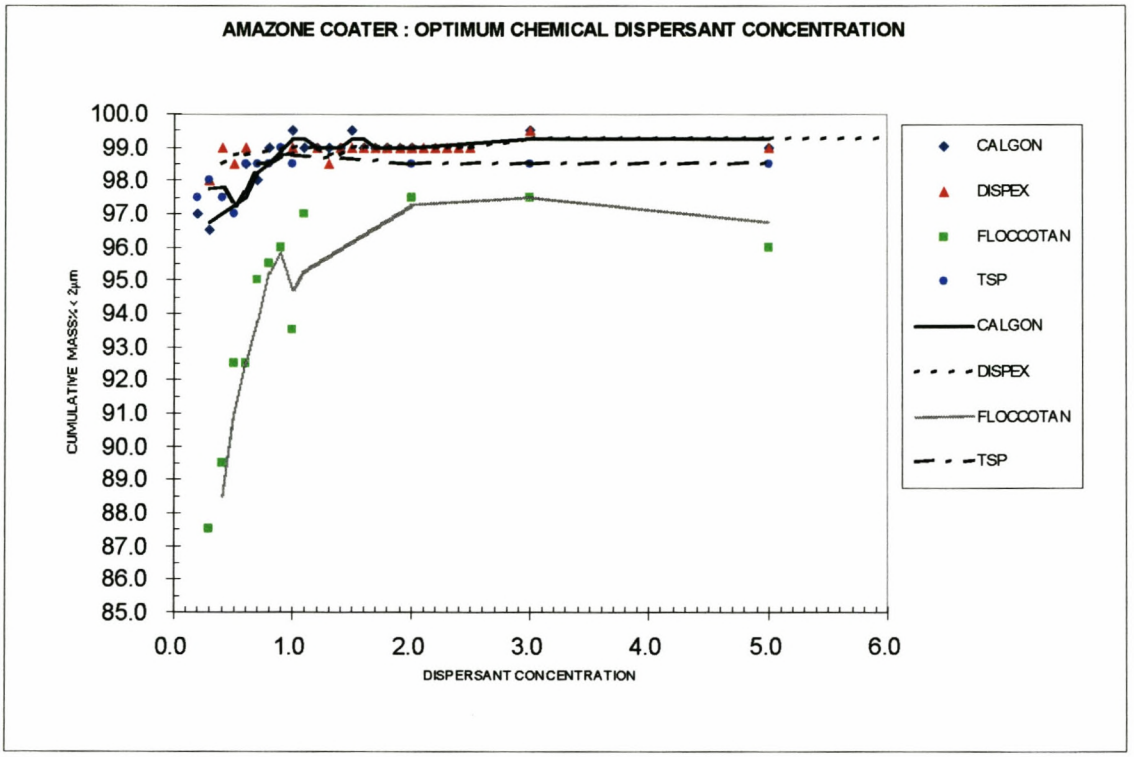


Table 4.1.2.1.2 (d). Dinkey filler

CALGON		DISPEX		FLOCCTAN	
DISPERSANT CONC. (%)	Cmp < 2 µm Done immediately after 3 min. ultras.	DISPERSANT CONC. (%)	Cmp < 2 µm Done immediately after 3 min. ultras.	DISPERSANT CONC. (%)	Cmp < 2 µm Done immediately after 3 min. ultras.
0	unstable	0	unstable	0	unstable
0.1	50.0	**0.1**	**50.0**	0.1	46.5
0.2	51.5	0.2	50	0.2	49.5
0.3	**50.0**	0.3	50	**0.3**	**50.0**
0.4	-	0.4	50	0.4	-
0.5	-	0.5	-	0.5	50.0
0.6	50.0	0.6	-	0.6	-
0.7	-	0.7	50	0.7	-
0.8	-	0.8	-	0.8	49.5
0.9	-	0.9	-	0.9	-
1.0	50.0	1	48.0	1.0	-
1.1	-	1.1	-	1.1	-
1.2	49.0	1.2	47.5	1.2	47.5
1.3	49.5	1.3	-	1.3	-
1.4	48.0	1.4	-	1.4	-
1.5	47.0	1.5	-	1.5	45.0
1.6	48.5	1.6	-	1.6	-
1.7	48.0	1.7	-	1.7	42.5
1.8	48.5	1.8	-	1.8	-
1.9	49.0	1.9	-	1.9	44.5
2.0	-	2.0	-	2.0	-
2.1	-	2.1	-	2.1	43.5

– : No particle size analysis done at the given dispersant concentration.

Fig. 4.1.2.1.1 (d). Dinkey filler

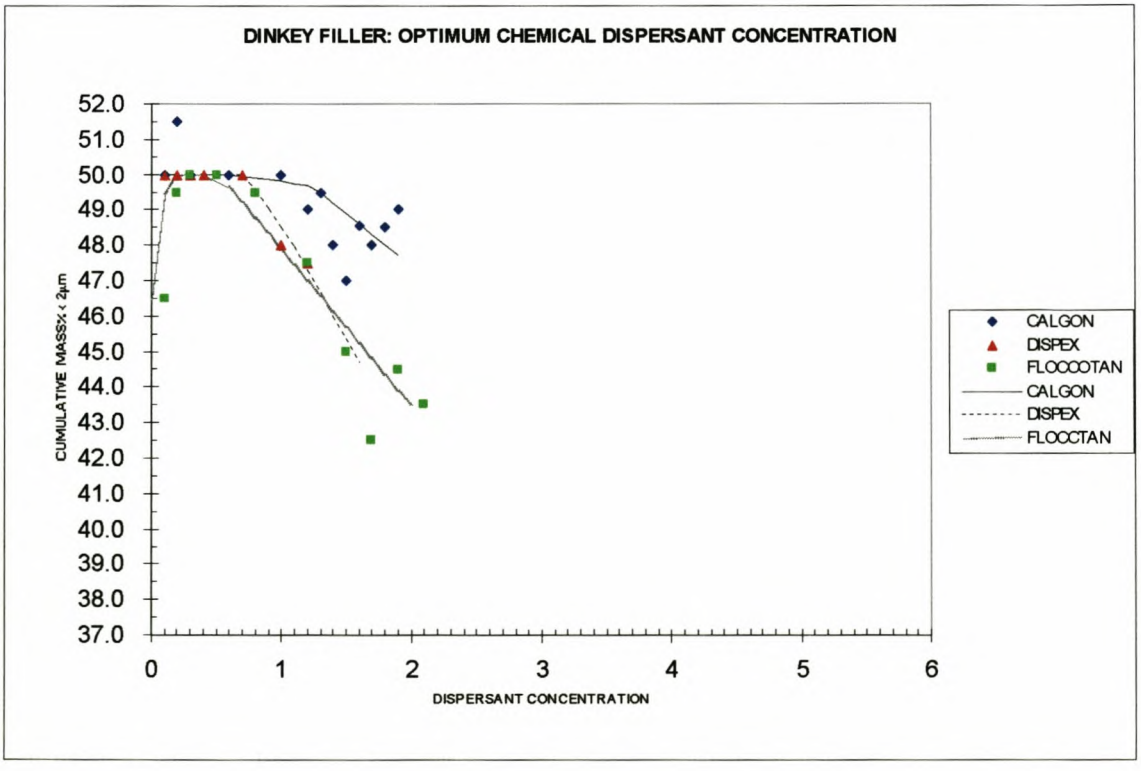
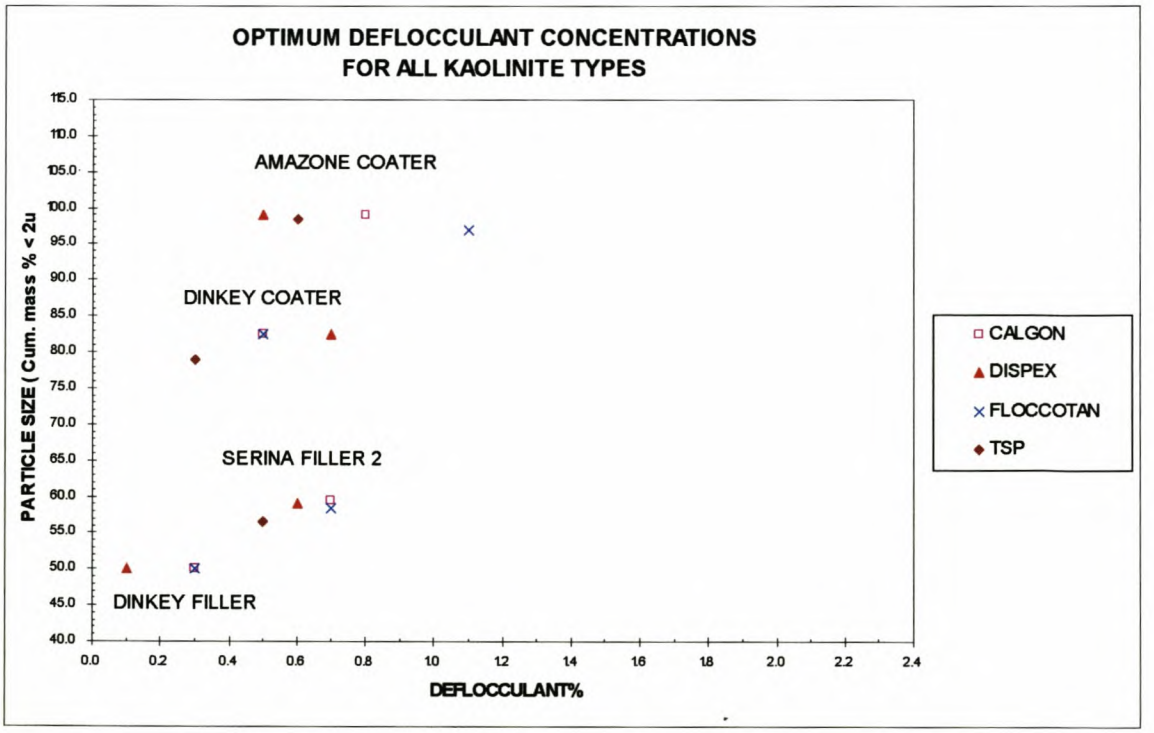


Table 4.1.2.1.3. Summary of the optimum deflocculant concentrations for Serina, Dinkey and Amazone using Calgon, Dispex and Floccotan.

DEFLOCC. CONC. %	CLAY TYPE	Cmp < 2 µm	CLAY TYPE	Cmp < 2 µm	CLAY TYPE	Cmp < 2 µm	CLAY TYPE	Cmp < 2 µm
	CALGON		DISPEX		FLOCCOTAN		TSP	
0.1			DINKEY FILLER	50.0				
0.2								
0.3	DINKEY FILLER	50.0			DINKEY FILLER	50.0	DINKEY COATER	79.0
0.4								
0.5	DINKEY COATER	82.5	AMAZONE COATER	99.0	DINKEY COATER	82.5	SERINA FILLER 2	56.5
0.6			SERINA FILLER 2	59.0			AMAZONE COATER	98.5
0.7	SERINA FILLER 2	59.5	DINKEY COATER	82.5	SERINA FILLER 2	58.5		
0.8	AMAZONE COATER	99.0						
0.9								
1.0								
1.1					AMAZONE COATER	97.0		

Fig. 4.1.2.1.2.



Tables 4.1.2.1.2 (a) – (d) thirdly reveal that, with the addition of deflocculant above the minimum amount necessary to effect dispersions, deflocculation improved even further. At length a plateau of constant cmp values is reached. For the four kaolinites, the start of these plateau values ranged between 0.1% and 1.1%. These points are defined here as the optimum dispersion concentrations.

However, for only one kaolinite, Dinkey filler, the plateau did not remain constant. Above critical deflocculant concentrations Dinkey filler gradually returned to less stable suspensions. This response to excessive deflocculant addition is defined here as over-deflocculation. With Dinkey filler the critical over-deflocculation value for Calgon is 1.2%, for Dispex it is 1.0%, and for Floccotan 0.8%.

Moreover, for only one kaolinite, Amazone coater, soaking prior to ultrasonic treatment was necessary before optimum dispersion could be achieved. When ultrasonic treatment was done on the Dispex samples, a relatively large amount of deflocculant was necessary to reach optimum dispersion (1.8% Dispex). After 3 days of soaking, only shaking to re-suspension gave no decrease in optimum dispersion concentration. Additional ultrasonic treatment after soaking, however, greatly decreased the optimum Dispex concentration from 1.8% to 0.4%. This indicates that many agglomerates are left over after the first ultrasonic treatment. Furthermore, to ensure successful ultrasonic treatment, agglomerates first need to be softened by soaking. This is confirmed by the fact that soaking before ultrasonic treatment facilitated optimum dispersion at lower deflocculant concentrations with most of the Amazone samples. Three days of soaking prior to ultrasonic treatment seem to be enough to provide Amazone coater with optimum stability. Of the four dispersants, Dispex gives the impression of benefiting de-aggregation best.

The data also yielded a useful pattern to demonstrate the relative competence of the four different deflocculants: Calgon, closely followed by Dispex, were the best deflocculants for all kaolinites. The difference in efficiency between the top two deflocculants was at the most only 0.5% cmp (the case of Serina filler – see Table 4.1.2.1.3).

The second best deflocculants were Floccotan and TSP. They were considerably less effective. For example: when Floccotan was used with both Amazone coater and Serina filler it gave 2% and 1% lower cmp values, respectively. TSP, with both Dinkey coater and Serina filler, gave 3.5% and 3.0% lower cmp values, respectively, than the best two deflocculants.

Conclusions:

1. Failure to disperse clays on, or above, an optimum deflocculant concentration will lead to inaccurate results. The optimum deflocculant concentration depends on the specific kaolin/deflocculant combination.
2. Under certain circumstances, the deflocculant concentration may affect the repeatability and reproducibility of the results. This will happen when deflocculant concentrations, while below optimum, differs from one analysis to the next (see Tables 4.1.2.1.2 (a) – (d)). Hence, working at a deflocculant concentration on, or above the optimum concentration would improve both accuracy and reproducibility.
3. The results confirm that as the degree of fineness of kaolinites increases, the amount of deflocculant to secure optimum dispersion also increases.
4. Calgon, closely followed by Dispex, was the best deflocculant for all four kaolinites tested. To promote the softening of aggregates due to soaking, Dispex is the best option. Floccotan and TSP were noticeably less efficient in contributing to the softening of aggregates.
5. For kaolinites to be safely dispersed, they should be slightly *over-deflocculated* above their optimum deflocculant concentrations. It is therefore recommended that Serina filler, Dinkey coater and Amazone coater be dispersed at a standard deflocculant concentration of 1.5%, regardless of deflocculant type. This will cause no problems with accuracy, since the cmp values of these kaolinites stayed constant even when dispersed to a 5% deflocculant concentration.

   However, in the case of Dinkey filler over-dispersion above a critical value led to less stable suspensions. The critical instability values of Dinkey filler lay between 0.5% and 0.8% past its optimum deflocculant concentrations – depending on the deflocculant type. Therefore, with all deflocculants, Dinkey filler must be over-dispersed with nothing more than 0.4% past the optimum deflocculant concentration.
6. The possibility that a clay can be under- and over-deflocculated suggests that a standardized deflocculant concentration must be very carefully chosen. Based on the above, 0.7% Dispex is suggested as a standard deflocculant concentration for all clays. The safest option, though, before attempting routine particle size analyses, is to first determine the optimum deflocculant concentration for every clay/deflocculant combination.

Recommendation for further study:

A study by Järnström and Stenius (1990) disclosed that Ca^{2+} saturation of a suspension, stabilised with a combination of Dispex and carboxy-methyl-cellulose, brought about more deflocculant adsorption. They postulated that the Ca^{2+} cations saturate the carboxylate polyacrylate anions to facilitate better adsorption to the less favourable adsorption sites on the basal surfaces.

On this account, it is suggested to determine optimum deflocculant concentrations at several Ca^{2+} concentrations, but this time in the presence of carboxy methylcellulose. This should be done with all the deflocculants.

4.1.2.2 Aiding chemical deflocculants by increasing the pH with Na_2CO_3

As the pH of a clay suspension is increased, there is a rapid expansion of the (–) surface charge density as it passes the pH value at the p.z.c. of the clay edges (section 1.5.5.1.2). This rapid expansion of surface charge density is not only due to the reversal of positive edge-charges to negative charges, but most likely also due to adsorption of OH^- on the basal surfaces (Street and Buchanan, 1956).

The reversal of the edge-charge leads to a net negative charge over all particle surfaces, and therefore to the break-up of edge-to-face bonds. Added to that, the higher (–) surface charge will induce the widening of the double layers. Consequently, the combined effect of both these effects should cause the amplification of repulsive forces. Hence the rise in pH past the p.z.c. at the clay edges results in the advancement of suspension stability.

Adding a deflocculant also enlarges the negative surface charge along the edges. Since increasing the pH does the same, but also adds negative charge to the much larger basal surfaces, it was reasoned that combining a deflocculant with a rise in pH might have a synergetic effect on clay stability. But, on the other hand, the OH^- anions and the polyanions of the deflocculant might compete for the positive surface charges – with unknown effect.

On these grounds it was decided to investigate whether, in the presence of each of the deflocculants used during this study, increasing the pH of kaolinite to beyond the p.z.c. at the edges (pH 7) will improve deflocculation. Na_2CO_3 was used since it also buffers the suspension against any change in pH that might be produced, for instance, by ambient CO_2 dissolving in the suspension liquid.

An added benefit in using Na_2CO_3 to enlarge the pH is that it simultaneously enhances the

amount of Na^+, which in turn adds to improved dispersion (section 1.5.5.2).

Materials and Methods:

In order to investigate the effect of increasing the pH with Na_2CO_3 in the presence of a deflocculant, three Serina filler samples were made up with Calgon, Dispex, and Floccotan. All were at 1% deflocculant concentrations, since it would ensure a safe degree of over-dispersion for all of them.

After soaking overnight, the samples were given a standard 3 min. ultrasonic treatment each. The pH of each was determined, and their particle size analyses conducted immediately.

After the first analysis was completed, the pH of each sample was stepwise increased by adding Na_2CO_3, until a pH of 9.5 was reached. The highest pH was chosen at 9.5, since at pH values higher than this clay dissolution can result (Oakley, 1927b). Due to their larger relative surface area this will especially be the case with the smallest clay particles.

The initial pH values for all of the three dispersants were acidic. Besides this, the initial pH also differed from one deflocculant type to the next. The pH with Floccotan was 4.98, for Calgon 5.79, and for Dispex the pH was nearly neutral at 6.92.

The results are tabulated in Tables 4.1.2.2.1 (a) – (c). The differences between the cmp values at higher pH values and that at the original pH were calculated (see Fig. 4.1.2.2.1 (a) – (c)), and their averages computed.

Results and Discussion:

For Calgon all the pH values above 7.00 gave better results than its initial pH of 5.78. The latter samples gave lower cmp values at some of the largest particle sizes, but higher cmp values in the smallest particle sizes. This resulted in smaller cmp differences for larger particles, and bigger cmp differences at the smaller particle sizes. This pattern indicates improved deflocculation at higher pH values. Flocks measured along with the larger particle sizes at lower pH, broke up under higher pH. Hence, the larger esds decreased in cmp, while the smaller particles freed from flocks increased the cmp of the smaller esds. The smallest particles (1 μm) experienced the largest increase in the cmp values, which gives a clear indication of the improvement in deflocculant efficiency.

Surprisingly, with Calgon the pH more or less on 7.00 (the p.z.c. at the edges in distilled water) gave the largest improvement in deflocculation. At pH 7.00 the cmp below 1 μm was 3.0% higher than at the initial pH of 5.78. But at pH 8.0 and pH 9.5 the cmp below 1 μm was

only 1.1% higher (Fig. 4.1.2.2.1 (a)). The average cmp values for all particle sizes echo that, despite the occasional negative values.

Table 4.1.2.2.1. The effect of the increase in pH on kaolinite particle size with three different deflocculants

(a) CALGON 1.0%

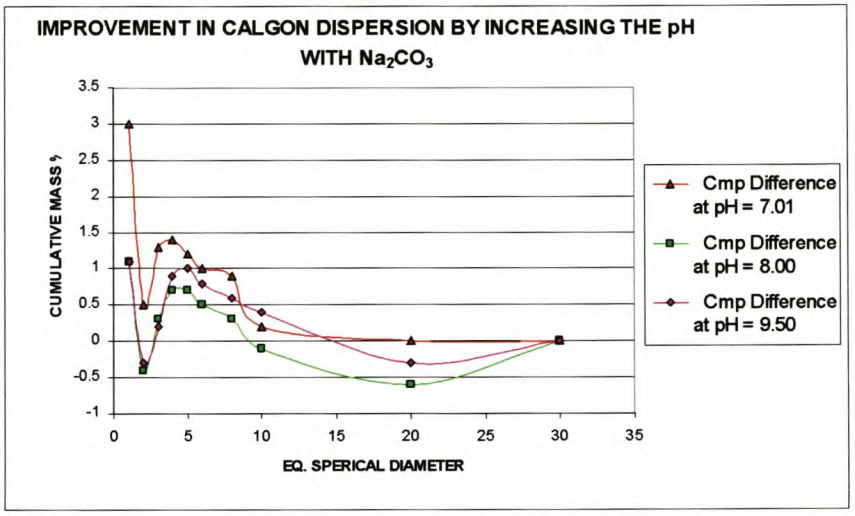
EQ. SPH. DIAMETER (μm)	CUMULATIVE MASS PERCENTAGE						
	pH = 5.78	pH = 7.01	Cmp Difference at pH = 7.01	pH = 8.00	Cmp Difference at pH = 8.00	pH = 9.50	Cmp Difference at pH = 9.50
30	100.0	100.0	0.0	100.0	0.0	100.0	0.0
20	100.0	100.0	0.0	99.4	-0.6	99.7	-0.3
10	94.4	94.6	0.2	94.3	-0.1	94.8	0.4
8	90.6	91.5	0.9	90.9	0.3	91.2	0.6
6	85.3	86.3	1.0	85.8	0.5	86.1	0.8
5	81.2	82.4	1.2	81.9	0.7	82.2	1.0
4	76.1	77.5	1.4	76.8	0.7	77.0	0.9
3	68.8	70.1	1.3	69.1	0.3	69.0	0.2
2	59.2	59.7	0.5	58.8	-0.4	58.9	-0.3
1	44.3	47.3	3.0	45.4	1.1	45.4	1.1
Average:			1.1		0.3		0.5

(b) DISPEX 1.0%

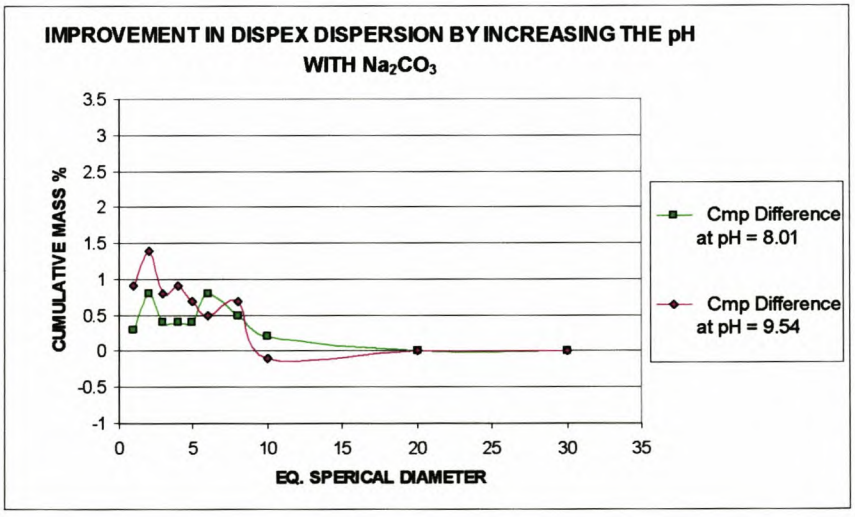
EQ. SPH. DIAMETER (μm)	CUM. MASS PERCENTAGE				
	pH = 6.92	pH = 8.01	Cmp Difference at pH = 8.01	pH = 9.54	Cmp Difference at pH = 9.54
30	100.0	100.0	0.0	100.0	0.0
20	100.0	100.0	0.0	100.0	0.0
10	94.3	94.5	0.2	94.2	-0.1
8	90.1	90.6	0.5	90.8	0.7
6	84.7	85.5	0.8	85.2	0.5
5	81.1	81.5	0.4	81.8	0.7
4	75.4	75.8	0.4	76.3	0.9
3	68.3	68.7	0.4	69.1	0.8
2	57.6	58.4	0.8	59.0	1.4
1	44.2	44.5	0.3	45.1	0.9
Average:			0.4		0.6

Fig. 4.1.2.2.1). The effect of a rise in pH on kaolinite particle size with three different deflocculants

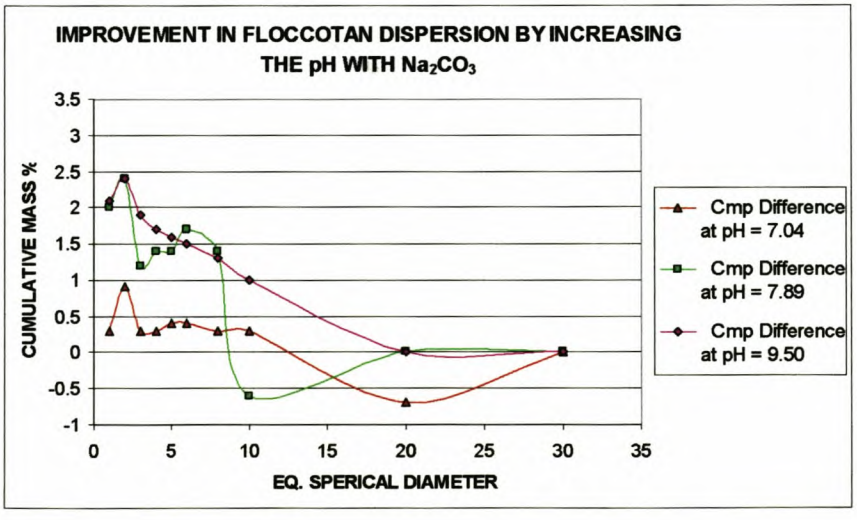
(a)



(b)



(c)



For the Dispex and Floccotan samples with pH values more or less at 7.00, only slightly better dispersion were obtained than at the initial pH. However, their highest pH values gave the best results. At pH 9.5 the cmp for Dispex at 1 μm was 0.9% better than that of its initial pH value (Fig. 4.1.2.2.1 (b)). The best dispersion for Floccotan was likewise attained at pH 9.5, with a 2.1% higher cmp at 1 μm than at the initial pH value (Fig. 4.1.2.2.1 (c)). The average cmp values follow the same pattern.

The reason why Calgon had its largest improvement in deflocculation at a pH 7.00 (just below the p.z.c of the clay edge) as opposed to the higher pH values as to be expected, is unclear (section 1.5.5.2).

Conclusions:

1. To achieve optimum chemical dispersion the pH of all kaolinite suspensions need to be adjusted to higher pH values by means of Na_2CO_3. With Calgon it needs to be adjusted to pH 7, and for Floccotan and Dispex to pH 9.5.
2. Floccotan benifits most from an increase in pH to 9.5 with Na_2CO_3.
3. Excess Na_2CO_3 in the presence of Calgon, causing pH values higher than 7.00, will lead to less improvement of kaolinite suspension stability.

Recommendation for further study:

Determine the optimum deflocculant concentrations of all clay/deflocculant combinations at various pH values, adjusted with Na_2CO_3. Obtain this for as many as possible single clay samples and soils. Determine both the minimum deflocculant concentration to optimally disperse them, as well as the concentration at which each will be over-deflocculated. From amongst these values of all of them, confirm whether the standard deflocculant concentration of 0.7%, proposed in the previous section, is applicable to all clays and soils.

4.1.2.3 Efficiency of using only desalination and high pH to effect deflocculation

The next step was to explore whether only increasing the pH of a clay suspension to above the p.z.c. at the edges in distilled water would disperse it as efficiently as when using a deflocculant. If successful, the use of a deflocculant could be eliminated. Along with it, the accompanying huge increase in Na-montmorillonite particle size due to swelling, and its decrease in particle size caused by delamination into single unit-layers when agitated, can also be avoided. Additionally, the collapse of Ca-montmorillonite to a smaller particle sizes can be

eliminated (section 1.5.8.2.2).

However, when using only a high pH to disperse a clay mixture, the effect of soluble salts present in natural samples must also be taken into account. As the salt content increases past a lower limit, the pH at the p.z.c. increases along with it (section 1.5.5.1.2). Therefore, the safest option is to first remove any soluble salts with centrifugal washing; thereafter, raise the pH to as high above 7 as possible without starting to dissolve the clay. Therefore, after removing all soluble salts, a pH of 9.5 would be sufficient. At pH values higher than 9.5, alkaline dissolution of the smallest clay particles will begin take place, which will artificially decrease the particle size.

The following test was devised to show whether the removal of salts by the standard method of centrifugal washing, followed by an increase of pH to 9.5, will be enough to effect complete dispersion.

Materials and Methods:

To rid four Serina filler 1 samples of all dissolved salts, they were centrifugally washed twice with water, after heating the suspensions to 80 °C. The samples deposited at the bottoms of centrifuge tubes were re-suspended between the two washings. After the last washing, all suspensions tested negative for dissolved Cl^- with 0.01M $AgNO_3$.

After the second centrifugal washing, two of the samples were then made up to 1.91% by volume, which is the lowest solids that could be tested on the apparatus used (section 4.2.2.2). The first one of these where re-suspended with distilled water only, and the second with distilled water plus 1.0% Dispex. The remaining two samples were dispersed in the same two ways, but at 3.85% by volume, which is the lowest solids to satisfy the Sedigraph handbook instructions (section 4.2.2.1).

Next, the two water-only samples were given the standard 3 min. ultrasonic treatment, where after their suspension pH was adjusted to 9.5 to try to accomplish deflocculation (called the pH only samples). This pH is safely above that at the p.z.c. of the edges. The two Dispex samples were also ultrasonicated, and adjusted to pH 9.5. Hence, they could be used as controls against which to test the effectiveness of the attempted deflocculation of the pH only samples.

Thereafter a particle size analysis was conducted immediately on each sample (Table 4.1.2.3.1).

Table 4.1.2.3.1. Testing the possibility of deflocculating a kaolinite sample by only increasing the pH (no deflocclant used)

All samples was desalinated prior to size analysis by means of centrifugal washing with distilled water.

EQ. SPH. DIA. (μm)	CUMULATIVE MASS PERCENTAGE			
	1.91% Solids		3.85% Solids	
	pH Only	Dispex 1.0%	pH Only	Dispex 1.0%
	Initial pH = 5.56 Adjusted pH = 9.52	Initial pH = 7.55 Adjusted pH = 9.51	Initial pH = 5.18 Adjusted pH = 9.51	Initial pH = 7.43 Adjusted pH = 9.5
1	Unstable	49.3	Unstable	47.4
2		61.0		60.4
3		70.7		70.6
4		76.8		77.1
5		81.4		82.0
6		85.1		85.9
8		90.4		91.0
10		93.2		94.3
20		100.0		100.0
30		100.0		100.0

Results and Discussion:

The pH-only samples at both 1.91% and 3.85% by volume were both completely unstable. They showed the characteristic signs of instability of suspension sticking to the sides of the sample holders exhibiting rivulets, and a plotter graph that stayed just below the 100% cmp line past 2 μm, showing cmp undulations of between 3.5% and 5.5% (section 4.2.3.1). It is evident that when deflocculation was attempted by raising the pH, the suspension was still completely unstable. On the other hand, at 2 μm the same kaolinite deflocculated with Dispex 1.0% gave cmp values of 49.4% and 47.4%, respectively, for the 1.91% and 3.85% by volume samples.

Conclusions:

1) Desalination plus increasing the pH to 9.5 was not effective to deflocculate the suspensions of water-washed kaolinite samples at the solid concentration range that could be tested with the apparatus used (1.91% to 3.85% by volume).

2) It is suspected that the solid concentration could be a major contributer to the instability observed, even at the high pH of 9.5. It was concluded that the reason for this is probably

that the higher the solid concentration, the closer the particles are to each other. Consequently, the amount of collisions due to the thermal movement of smaller particles will be greater. Hence, the smaller the particle size, the higher the chance of flocculation.

4.1.2.3.1 The influence of solid concentration on the degree of instability

To test if high solid concentration was truly a cause for the instability during the previous test despite desalination and the high pH of 9.5 (section 4.1.2.3), a second experiment was devised to verify this. Five kaolinite suspensions of Serina filler 1, with increasing solid concentrations of 0.3%, 0.6%, 1.91%, 2.80%, and 3.85% by volume, respectively, was made up at pH 9.5. As the highest solid concentration, 3.85% by volume was chosen. This is the solid concentration above which the minimum requirements of the Sedigraph 5000D was still satisfied (section 4.2.2.1). As the lowest concentration, the 0.6% solids sample was included, since this is the approximate clay concentration of the Andreasen pipette method. Hence, this test would additionally compare the accuracy of the two sedimentary methods when using this approach to deflocculation.

Materials and Methods:

Instead of using Sedigraph particle size analysis, a sedimentation test in glass beakers was employed. The reason was that beneath a solid concentration of 1.91% by volume, accuracy with the Sedigraph 5000D decreases to below acceptable levels (section 4.2.2.2). However, when using a sedimentation test, the solid concentrations could be decreased to 0.3%.

To eliminate any chance that soluble salts or methanol could induce flocculation, all the samples were centrifugally washed three times in distilled water. During centrifugal washing, the samples need to be flocculated to facilitate deposition at the bottom of the tubes. However, with repeated washing with water, samples increasingly become un-flocculated due to salt removal. Therefore, to still provoke flocculation in water, the samples were first heated in a water-bath for about 20 min. (section 1.5.5.1.2). This allowed enough time to reach the highest achievable suspension temperature of 80 °C. This temperature was high enough to ensure flocculation of even the smallest particles, ensuring complete sample retrieval at the final low salt content.

Although heating was successful in flocculating the sample, to completely deposit the samples between washings, a higher rpm than with methanol had to be used. As a consequence, re-suspending the more tightly packed samples from the bottoms of the centrifuge tubes took a lot more time and effort than was the case after the lower rpm washing

with methanol.

After the last centrifugal washing, the next step was to adjust the pH of the samples to 9.5 by means of Na_2CO_3, in an attempt to deflocculate them. Using Na_2CO_3 is a better option than NaOH, since the former buffers itself in the following manner:

$$Na_2CO_3 \rightleftharpoons 2Na + CO_3^{=} + H_2O \rightleftharpoons 2Na + HCO_3^{-} + OH^{-}$$

Should OH^- anions be removed in any manner, it is replaced due to the hydration of the remaining $CO_3^{=}$ ions in solution. Thus, the pH of a suspension is more stable.

While adjusting the pH to 9.5, the Na_2CO_3 powder was carefully added to the sample while agitating the sample with a magnetic stirrer. During any agitation, the pH of suspensions always registers by between 0.09 and 0.07 lower than that when static. Therefore, under agitation, the pH was first adjusted to more or less pH 9.41, and then the stirrer was switched off. After allowing it enough time to equilibrate, the pH value was noted – and more Na_2CO_3 added where necessary to obtain the required value. To make the last fine adjustments, an appropriate amount of 0.01M Na_2CO_3 drops was added. However, when overshooting the pH value of 9.5, a few drop of 0.01M HCl was used to reduce the pH again to a value right on, or close to 9.5. A large enough amount of HCl can cause destruction of the crystalline lattices of clay minerals (Gee and Bauder, 1986) especially if the pH is reduced to below 5.0. However, the very small amounts of HCl used in the above case, would probably not have caused this.

As a control to substantiate the stability of the pH-only-samples, five additional Serina filler 1 samples were made up at the same solid concentration. They, however, were dispersed with 1% Dispex. To be able to compare the sedimentation volumes and clay/water interfaces with that of the pH-only samples, the two series of samples were poured in same-sized glass beakers. All samples were then arranged such that the Dispex samples, and the pH 9.5 samples of same solid concentration, were right alongside each other.

After periods of 24 hours and 48 hours of standing, the sedimentation volumes and the height of the clay/water interfaces were measured with a ruler, and tabulated (Table 4.1.2.3.1.1).

Table 4.1.2.3.1.1. Comparison of the sedimentation volumes and the height of the clay/water interfaces of samples dispersed by Dispex deflocculant, or by only increasing the pH to 9.5.

SOLIDS CONC. (% by vol.)	MEANS OF DEFLOCCULATION	SEDIMENT HIGHT (mm)	CLAY/WATER INTERFACE DEPTH (mm)
3.85%	Dispex 1%	24 hr. = 6.2 48 hr. = 7.2	24 hr. = 0.0 48 hr. = 0.0
	pH 9.5 only	24 hr. = 46.0 48 hr. = 44.0	24 hr. = 6.8 48 hr. = 7.2
2.80%	Dispex 1%	24 hr. = 6.0 48 hr. = 6.9	24 hr. = 0.0 48 hr. = 0.0
	pH 9.5 only	24 hr. = 37.5 48 hr. = 35.2	24 hr. = 14.0 48 hr. = 16.2
1.91%	Dispex 1%	24 hr. = 5.4 48 hr. = 5.9	24 hr. = 0.0 48 hr. = 0.0
	pH 9.5 only	24 hr. = 31.0 48 hr. = 29.5	24 hr. = 23.0 48 hr. = 23.5
0.60%	Dispex 1%	24 hr. = 2.7 48 hr. = 2.2	24 hr. = 0.0 48 hr. = 0.0
	pH 9.5 only	24 hr. = 12.9 48 hr. = 12.0	24 hr. = 0.0 48 hr. = 0.0
0.30%	Dispex 1%	24 hr. = 1.9 48 hr. = 2.0	24 hr. = 0.0 48 hr. = 0.0
	pH 9.5 only	24 hr. = 7.9 48 hr. = 7.0	24 hr. = 0.0 48 hr. = 0.0

Results and Discussion:

Despite the adjustment of the pH to 9.5, the pH-only samples at the higher solid concentrations of between 1.91% and 3.85% were completely unstable: each exhibited a sharp clay water interface, with a clear supernatant overlying it. Moreover, the clay suspension below the interfaces was visibly flocculated, and displayed large sedimentation volumes. These prove substantial amounts of edge-to-face card-house structures. The results are consistent with those of same solid concentration of the previous section.

On the other hand, all the Dispex 1% samples of similar solid concentrations had thin, and very dense sediments. The thin, densely packed layers of sediment suggest that the platelets settled upon each other, with their large faces in parallel orientation. This suggests the total absence of edge-to-face bonds or card-house structures. Both the latter observations suggest complete deflocculation – even at the highest solid concentration of 3.85%.

A further clear proof of stability of the Dispex samples was that even after 48 hours none of them displayed clay water interfaces. The finest particles at the top of the suspensions had a

diffuse appearance, stretching right up to the water/air interface.

At 0.6% and 0.3% solids, the pH-only samples concentration had smaller sedimentation volumes than the 1.91% and 3.85% pH-only samples. These bottom layers of the pH-only samples were still flocculated to some degree, and still much higher than those of all the Dispex samples. However, in contrast to the clear supernatant of the 1.91% and 3.85% pH-only samples, both the lower solid concentration (0.6% and 0.3%) pH-only samples displayed some diffuse, un-flocculated particles above their flocculated bottom layers. In both the latter samples, though, these diffuse upper layers were visibly of lower clay concentration than those of their Dispex counterparts.

Hence, at the lower solid concentration of the Andreasen pipette method (0.6% by volume) and below, the increase in pH to 9.5 did in fact disperse some particles. But the smaller amount of diffuse deflocculated particles, and the wide flocculated bottom layers, prove that desalinating a clay suspension and increasing its pH, is by far not as effective to attain deflocculation as when Dispex is used.

The question now is why only the chemical deflocculant was effective, whereas raising the pH was unsuccessful. Both adding a deflocculant, as well as increasing the pH above the p.z.c. at the edges, reverse the positive edge-charge to negative charge, causing repulsion between edges and faces. Therefore, using either a deflocculant, or only raising the pH above that of the p.z.c. at the edges, should both in theory completely deflocculate a clay suspension.

The reason why this is not so probably lies in the fact that only some of the negative charges of the polyanion deflocculant molecules adsorb to the available positive surface charges, while most of the negative charges orientate outwards. Thus, a large amount of negative surface charge is effectively added to the clay surfaces. Therefore, much larger amounts of (+) Na-counter ions are attracted to the double layer than is the case when only the pH is increased. Hence, the much wider double layers thus created when using deflocculants, causes much stronger inter-particle repulsion than when only the pH is increased to bring about deflocculation. For the latter reason, when using only the increase in pH, the thinner double layers cannot stop collisions from moving particle surfaces close enough together, and van der Waals attraction can take over. Hence, edge-to-face bonds more readily form – especially when particles are close together at the higher solid concentrations of 1.91% and above.

However, at lower solid concentration there is less chance of strong enough collisions since the particle will on average be spaced further apart. This especially the case with smaller

particles, since they encounter larger Brownian movement. Therefore, in the pH-only samples, flocculation decreases somewhat when lowering the solids content, but it was still present to a significant extent. When compared to the Dispex samples, the flocculation in the pH-only samples therefore brought about the observed large sedimentation volumes, and smaller amounts of particles suspended above it.

Conclusions:

1) At solid concentrations on, or above 1.91% by volume, a too high solids content was a major contributor to the inability to disperse kaolinite only by desalination followed by increasing the pH (section 4.1.2.3). This is proven by the sharp clay/water interfaces of the higher solid concentration samples, overlain by a clear supernatant.

2) Despite the removal of excess soluble salts, and the reversal of kaolinite edge-charge by increasing the pH to above 9.5, the singly charged double layers acquired in this way are not wide enough to facilitate complete dispersion in distilled water. De-salination and raising the pH are therefore by far not effective enough to replace deflocculants when attempting to disperse clays for particle size analysis.

   Both Na- and Ca-montmorillonite therefore need to be deflocculated by a chemical deflocculant, if particle size analysis is attempted on either. But a deflocculant causes larger swelling of Na-montmorillonite than in nature, and fully collapses Ca-montmorillonite. Hence, neither of these montmorillonites will ever, by any dispersion method, yield their natural particle sizes during particle size analysis in water.

3) Heating to effect flocculation during centrifugal washing is a tedious operation. It takes a long time to raise the sample temperature to a maximum of 80 °C. The higher rpm needed to deposit these samples, leads to a longer duration to re-suspend the sample from the bottoms of centrifuge tubes. Therefore, centrifugal washing with heated distilled water should only be employed in the place of ethanol and methanol, when the presence of these organic solvents is for some reason undesirable.

Suggestions for further study:

The downside of using a sedimentation test in place of Sedigraph analysis is that if a suspension is deflocculated only by desalination and increasing the pH, then "stability" is a relative term. In fact, the degree of stability, or instability, of a sol is defined in terms of its coagulation rate (van Olphen, 1977). In contrast to the case with chemical deflocculants, flocks always a start to grow when a desalinated pH-only suspension is left standing after

agitation. The rate of flock-growth is slow in "stable" sols, and *visa versa*.

During the above test, the pH-only sample was left standing for hours to allow the differentiation of particle sizes to become visually discernable in the suspension. The 24 hours given for the first comparison between pH-only samples and Dispex samples could therefore have allowed enough time for substantial amounts of flocculation in the former. This test therefore does not necessarily exclude the use of desalination and increase in pH to affect deflocculation: Successful deflocculation to permit accurate Sedigraph analysis with pH-only samples might still be achieved, if conducted just after the suspension is made up. In this way the severe modification by deflocculants of the particle size of both Ca- and Na-montmorillonite might still be avoided.

It is therefore suggested to repeat the comparison between a sample dispersed with Dispex and one dispersed only with desalination and the increase in pH. But this time use the Sedigraph to reduce the time for flock growth to only 12 min. The samples must be made up at the lowest solid concentration the Sedigraph can handle (1.91% by volume), and the analyses must be conducted immediately after ultrasonic treatment and shaking is completed.

To get an idea of the accuracy of these analyses: compare their particle size distributions of both 1.91% solids samples with that of a Dispex sample conducted at 3.85% solids by volume (the solid concentration answering to the minimum instrument requirements for accurate analysis with the Sedigraph – section 4.2.2.1).

4.1.3 Implications of wrong grinding technique and improper ultrasonic treatment

The two most important factors playing a role in the efficiency of de-agglomeration and de-aggregation during ultrasonic treatment are: the strength of the binding material, the duration of ultrasonic treatment. Added to that are the factors dealing with the suspension: particle size distribution, volume, solid concentration, salt concentration, deflocculant concentration, and stirring. Making up the rest of the parameters are the liquid properties: volume, viscosity, liquid temperature, depth, pressure, and gas content; and the two parameters dealing with the equipment *viz.* the Watt and KHz. of the sonic vibrator (section 1.5.7.4).

The potential detrimental effect on accuracy and reproducibility of the last five variables can only be investigated by means of an ultrasonic probe with variable Watt and Hz. Such an instrument, however, was not available for this study. Hence, a normal ultrasonic bath was used.

The effects on accuracy and reproducibility of only two variables were studied *viz.* the duration of ultrasonic treatment, and the influence of stirring during the cause of the treatment. The suspension's solid concentration, viscosity, salt concentration, deflocculant concentration, and particle size distribution are all fixed by other factors during Sedigraph analysis, and was therefore not investigated.

4.1.3.1 The combined effect of intensity of grinding and duration of ultrasonic treatment

Besides ultrasonic treatment, the milling in a mortar and pestle preceding it can modify the clay particle size through the break-up of agglomerates, aggregates, and single particles. For this reason an experiment was designed to demonstrate simultaneously the effect of both grinding and ultrasonic treatment on accuracy, repeatability, and reproducibility.

With ultrasonic treatment, the duration affects the amount of break-up. With the mortar and pestle, it is the intensity of grinding that matters. Therefore, to investigate the potential negative effects of both ultrasonic treatment and grinding on accuracy and reproducibility, different samples were first exposed to varying intensities of grinding. It was then followed by different durations of ultrasonic treatment.

Materials and methods:

Three kaolinite types were used: the coarser Dinkey filler, middle-sized Serina filler 2, and the finer Amazone coater. Three samples were prepared of each kaolinite type.

The first sample of each was lightly ground in mortar and pestle. Enough clay was ground at a time to make certain that there was always a thin layer of kaolinite of at least 2 mm thick between mortar and pestle. The permanent clay layer assured that no particles were crushed due to direct contact between their hard surfaces. This would minimise splitting along the {001} cleavage planes. In addition, grinding was conducted lightly to reduce breakage perpendicular to basal surfaces due to particle rotation. Both types of breakage would reduce the amount of bigger particles, and add to the amount of smaller ones.

The second samples were ground with more force than the first ones. This time much less sample was used (±1g), so that the pestle frequently ground through the clay layer onto the hard mortar surface. Grinding was continued until no aggregates could be felt between the fingers.

Table 4.1.3.1.1. Determination of optimum ultrasonic time (plateau values), in an ultrasonic bath, for Serina filler, Dinkey filler 2, Serina and Amazone coater.

Dispex 1.3% was used as dispersant. Particle sizes in bold correspond to the chosen optimum ultrasonic time (plateau value).

(a) Dinkey filler

ULTRASONIC TIME (min.)	CUMULATIVE MASS% < 2 µm					CUMULATIVE MASS% < 1 µm			
	UNGROUND	ERROR	GROUND	HEAVILY GROUND	ERROR	UNGROUND	ERROR	GROUND	HEAVILY GROUND
0.0	46.0		52.5	54.0		9.0		18.5	19.5
0.5	47.0		54.0	59.0		10.0		20.0	26.0
1.0	47.5		**55.5**	59.5		10.5		**21.5**	26.0
1.5	48.0		56.5	60.5		11.0		23.5	27.0
2.0	48.5		56.5	60.5		12.0		23.5	28.0
2.5	51.5		57.0	60.5		13.0		24.0	30.0
3.0	**51.5**	-5.5	57.0	62.0	5.0	**14.0**	-11.0	25.0	31.0
3.5	51.5		57.0	**62.0**		14.0		25.0	**32.0**
4.0	51.5		57.0	62.0		14.0		25.0	32.0
4.5	51.5		57.5	62.0		14.0		25.5	32.0
5.0	51.5		57.5	62.0		15.0		25.5	32.0
6.0	51.5		57.5	62.0		15.0		25.5	32.0
7.0	52.0		57.5	63.0		15.5		25.5	32.0
10.0	52.5		58.0	63.5		16.5		26.0	33.5
15.0	52.5		59.0	64.0		16.5		27.5	36.0
20.0	54.0		59.5	65.0		17.0		27.5	35.0
25.0	55.5		60.0	64.5		19.0		28.0	34.5

Table 4.1.3.1.1 (b). Serina filler 2

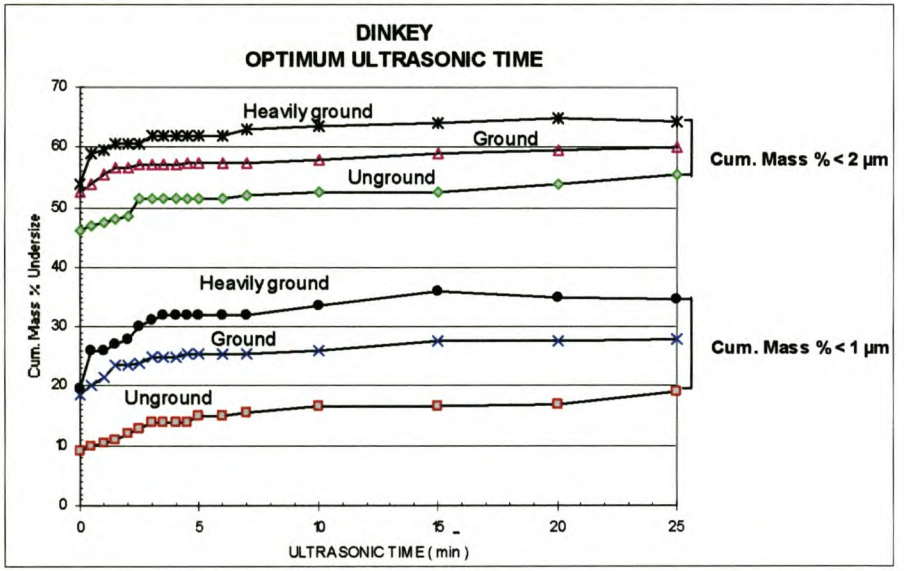
ULTRASONIC TIME (min.)	CUMULATIVE MASS% < 2 µm					CUMULATIVE MASS% < 1 µm			
	UNGROUND	ERROR	GROUND	HEAVILY GROUND	ERROR	UNGROUND	ERROR	GROUND	HEAVILY GROUND
0.0	54.0		56.5	59.0		38.5		41.5	43.0
0.5	56.0		58.5	60.5		40.5		43.5	45.5
1.0	57.5		**59.0**	61.5		42.5		**43.5**	47.0
1.5	58.0		59.5	62.0		43.0		43.5	47.0
2.0	58.5		59.5	62.5		43.5		43.5	47.5
2.5	58.5		59.5	62.5		43.5		43.5	47.5
3.0	**58.5**	-1.0	59.5	62.5	3.0	**43.5**	0.0	43.5	47.5
3.5	58.5		59.5	**62.5**		43.5		44.0	**47.5**
4.0	59.5		59.5	62.5		44.0		44.5	47.5
4.5	60.0		59.5	62.5		45.0		44.5	47.5
5.0	60.0		60.0	62.5		45.0		45.0	48.5
6.0	60.0		60.0	63.0		45.0		46.0	49.0
7.0	60.0		61.0	63.0		45.5		46.0	49.0
10.0	60.0		61.5	64.5		45.5		46.0	50.0
15.0	61.0		61.0	64.5		46.5		46.0	50.0
20.0	62.0		61.5	65.0		47.0		47.0	50.0
25.0	61.5		61.5	65.0		46.5		47.0	50.0

Table 4.1.3.1.1 (c). Amazone coater

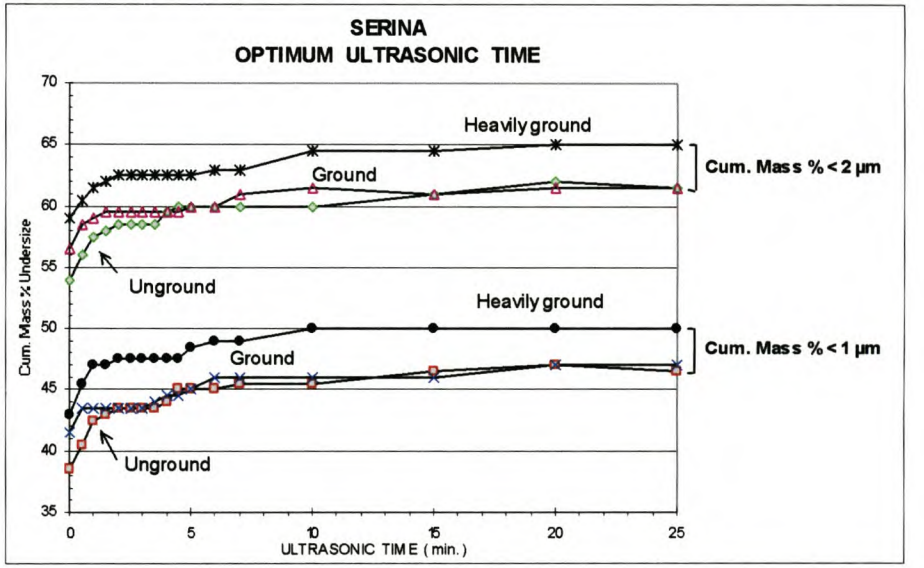
ULTRASONIC TIME (min.)	CUMULATIVE MASS% < 2 µm					CUMULATIVE MASS% < 1 µm			
	UNGROUND	ERROR	GROUND	HEAVILY GROUND	ERROR	UNGROUND	ERROR	GROUND	HEAVILY GROUND
0.0	Unstable*		68.5	96.0		Unstable		66.5	94.0
0.5	Unstable		98.0	100.0		Unstable		96.0	99.0
1.0	Unstable		**99.5**	100.0		Unstable		**97.0**	99.0
1.5	Unstable		99.5	100.0		Unstable		98.0	99.0
2.0	98.0		99.5	100.0		96.0		98.5	99.0
2.5	99.5		99.5	100.0		98.0		98.5	99.0
3.0	**99.5**	0.0	99.5	100.0	0.5	**98.5**	0.0	98.5	99.5
3.5	99.5		99.5	**100.0**		99.0		98.5	**99.5**
4.0	99.5		99.5	100.0		99.0		98.5	99.5
4.5	99.5		99.5	100.0		99.0		98.5	99.5
5.0	100.0		99.5	100.0		99.0		98.5	99.5
6.0	100.0		99.5	100.0		99.0		98.5	99.5
7.0	100.0		100.0	100.0		99.0		98.5	99.5
10.0	100.0		100.0	100.0		99.0		98.5	100.0
15.0	100.0		100.0	100.0		99.0		98.5	100.0
20.0	100.0		100.0	100.0		99.5		98.5	100.0
25.0	100.0		100.0	100.0		99.5		99.0	100.0

*Unstable means: Particle size determination done, but results inaccurate due to instability of the clay suspension at the given ultrasonic time.

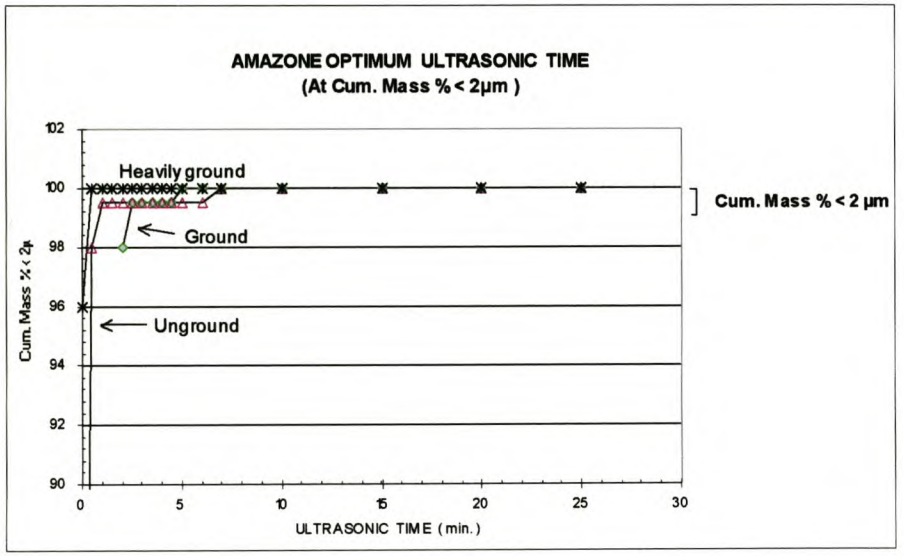
Fig. 4.1.3.1.1 (a). Dinkey filler



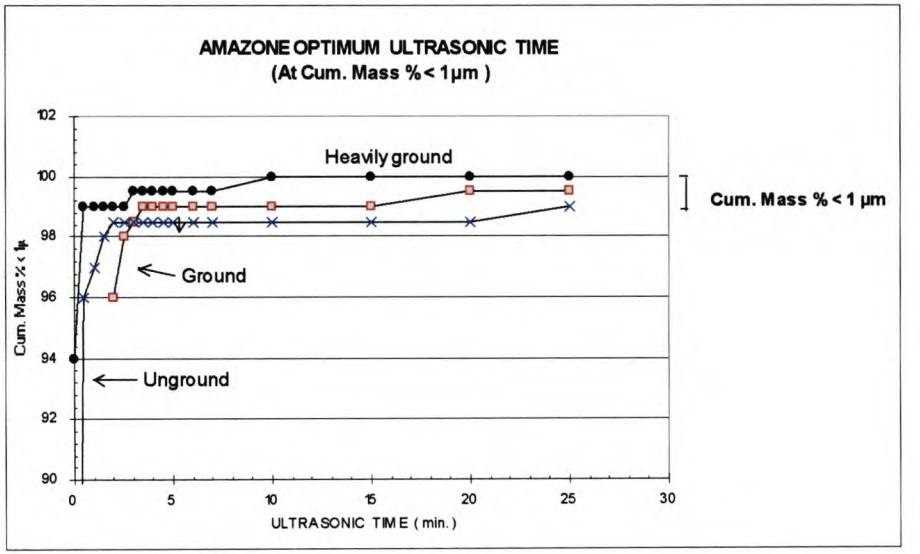
(b) Serina filler 2



(c) Amazone coater < 2 µm



(d) Amazone coater < 1 µm



The third samples were not ground at all. The un-ground, ground, and heavily ground samples for each kaolin type were suspended in distilled water containing 1.3% Dispex deflocculant.

Thereafter each sample was repeatedly sonicated in an ultrasonic bath, whilst stepwise increasing the cumulative ultrasonic time up to a total of 25 min. The ultrasonic treatment was carried out in the presence of the deflocculant to enhance the fragmentation of agglomerates (sections also 1.5.7.4 and 4.1.2.1).

The samples were analysed for particle size between each ultrasonic treatment. For each analysis the cmp smaller than both 1 μm and 2 μm are tabulated (Table 4.1.3.1.1 (a) – (c)), and presented visually in Figures 4.1.3.1.1 (a) – (d). The cmps below 2 μm and 1 μm were chosen because the smaller particle sizes would hold the products of fragmentation of agglomerates, aggregates, and single particles produced by the combined effect of grinding and ultrasonic treatment.The cmp errors were also calculated for samples that was not ground at all, as well as for the too heavily ground ones. This was accomplished by subtracting the cmp values of the ground samples, and those ground too heavily, from that of samples prepared with a supposedly proper soft grinding technique (Tables 4.1.3.1.1 (a) - (c)). The latter analyses were in all cases preceded by an ultrasonic treatment of 3 min.

Results and Discussion:

Tables 4.1.3.1.1 (a) - (c) and Figures 4.1.3.1.1 (a) - (d) first of all indicates that whether ground or not: the particle size reduced with the enlargement of ultrasonic time.

Contrary to the ultrasonic probe results of Watson (1970) and North (1976) (section 1.5.7.4), the ultrasonic bath results reveal that with longer ultrasonic time the cmp values exhibit two plateaus. Each plateau is preceded by a separate period during which the cmp rises to that of the next plateau. The values at which each kaolinite type reached the first cmp plateau is given in bold in Table 4.1.3.1.1.

With all samples, the first cmp plateau is reached within 3 min. or less. The second cmp plateau is reached for Serina filler and Amazone coater samples between 3 – 7 min. of ultrasonic treatment. The same is found with both the heavily and lightly ground Dinkey filler samples for particles <1 μm – but after longer durations of ultrasonic treatment. For the rest of the Dinkey filler samples, the cmp gradually continues to rise without reaching a second plateau – for them second plateaus might still be reached if the ultrasonic time is increased

beyond 25 min. (section 1.5.7.4).

At the 1 µm particle size for the heavily ground Dinkey filler and Amazone coater, an apparent third cmp plateau is reached with increased ultrasonic time. However, the periods of break-up before the apparent second plateau, though, is so short that the first two plateaus can be taken as one. The "third plateau" should therefore also be viewed as a second plateau.

In most cases the reason for the formation of two plateaus when increasing the duration of treatment in an ultrasonic bath is probably that the weaker agglomerates are easier to break up, whereas more ultrasonic energy is needed to do the same for the much stronger aggregates (section 1.5.7.4). At first, break-up of only the less resistant *agglomerates* leads to the observed rise in cmp with growing ultrasonic time before the first plateau is formed. When that is completed, the cmp stays constant for a while despite further increase in ultrasonic time. Thus the first plateau is formed.

Only after enough ultrasonic energy is added, the break-up of more resistant *aggregates* becomes enough to also become evident. Accordingly, the cmp starts to enlarge towards the second plateau. When aggregate break-up is completed, the second plateau of constant cmp is reached. Re-agglomeration might have drawn out the duration of the two periods of break-up before each of the two plateaus is formed (section 1.5.7.4).

In some cases the last plateau exhibits a slight, but continuously enlarging cmp value. This is probably due to ongoing break-up of remaining < 2 µm sub-complexes. This is because the more both the constituent particles and the smaller aggregates are abraded, the more the break-up process is slowed down (section 1.5.7.4).

A single cmp plateau was formed with the experiments of Watson (1970) and North (1976), which is contrary to the above results with the ultrasonic bath. The reason probably was that the ultrasonic probes they used were strong enough to break up the more resistant aggregates right from the start.

When further inspecting the results one notices that al priorly ground samples started at higher cmp values with their first ultrasonic treatment, than those without. This indicates that ultrasonic treatment alone produces less sufficient break-up of particle assemblies, than when combined with grinding.

However, with both Serina filler and Amazone coater: from 2-4 min. ultrasonic time onwards, even before the first plateau was reached, *lightly ground* and *un-ground* samples (ultrasonic treatment only) became broken up equally effectively. The most likely explanation

is that light grinding is capable to partially break up the *weaker agglomerates* of these two kaolinite types. As a result, the *ground* samples initially had higher cmp values at both 2 µm and 1 µm. But after being exposed to ultrasonic energy for long enough the agglomerate break-up of the *un-ground* samples caught up with that of the ground samples – sometimes even before the first cmp plateau was reached.

Light grinding, though, does not break up the more resistant aggregates of all kaolinites. This is proven by the fact that after the first plateaus of all kaolinites, the hard aggregates of both the *un-ground* and the *lightly ground* samples break up at the same pace under increasing ultrasonic time. They therefore reach the second plateau after completion of the same amount of ultrasonic time, proving that only ultrasonic treatment can break up the more resistant *aggregates*.

Moreover, when the *heavily ground* samples were investigated it was discovered that at 1 µm with Serina filler and Amazone coater the lightly ground and un-ground samples never reached the same cmp levels as the heavily ground samples (see Tables 4.1.3.1.1 (a) - (c) and Figures 4.1.3.1.1 (a) - (d)). This suggests that heavy grinding additionally breaks up *single particles*. But with light grinding, or with the ultrasonic bath on its own (the un-ground sample), single particles remained unbroken – even after 25 min. of ultrasonic treatment. Contrarily, with the heavily ground sample its second cmp plateaus for the smallest 1 µm particles starts higher since it contains the artefacts of single-particle break-up. However, the lesser intense treatments never caught up as ultrasonic time advanced, since they never produce single-particle break-up.

Surprisingly, heavily ground samples display the same pattern of initial increase in cmp before the first plateau is reached. This indicates that there are still weaker agglomerate*s* left over, even after heavy grinding with a small amount of clay.

In conclusion, when the errors in cmp are inspected, an interesting pattern immerges: with Dinkey filler the cmp errors were largest when it was *unground* prior to sonication. Contrary to this for Serina filler 2, when heavily ground, the errors were bigger at both particle sizes. And lastly, the errors for Amazone coater – surprisingly – were absent when unground, and much smaller than the other kaolinite types when heavily ground. This confirms that grinding alone does not break up some of the aggregates – additional ultrasonic treatment is needed for that. As with Serina filler 2 the Amazone errors were also largest at the heavily ground sample at 1 µm. In fact, with all clays the cmp errors were most pronounced at the smaller particle size of 1 µm.

Conclusions:

1. Since even heavy grinding cannot break up all the less resistant kaolinite *agglomerates*, ultrasonic treatment must always be conducted ahead of particle size analysis.
2. A kaolinite can have very resistant *aggregates*, which cannot be broken up by ultrasonic baths (like in the case of Dinkey filler). Therefore, if sizes of the particles contained in the harder type aggregates are of any importance, then *light* grinding in mortar and pestle should always precede ultrasonic bath treatment for all kaolinites.
3. Heavy grinding with small amounts of sample causes hard contact between mortar and pestle, which leads to single particles break-up. This must at all times be avoided since it leads to inaccurate particle size analysis results – especially for the smallest particle sizes. Light grinding, though, proved itself safe in this regard.

   On these grounds, only light grinding must precede weighing. It must be conducted with just enough pressure to break the clay down to sugar-sized lumps and smaller to allow accurate weighing. Additionally there must be enough clay in the mortar to prevent the pestle to grind through onto its hard surface.
4. The ultrasonic bath used during this study did not produce any single particle break-up to be noticeable in the analysis results – even at 1 μm. An ultrasonic bath can therefore safely be used in combination with light grinding.
5. Increasing ultrasonic time led to larger cmp values in the smaller particle sizes. This implies that to insure reproducibility, as well as comparability between operators, ultrasonic time needs to be standardised. Since with larger ultrasonic times aggregate break-up differs from one clay to the next, every clay type needs its own ultrasonic time.
6. It can take up to 40 min. of ultrasonic time before some clays level off to a single cmp plateau when using a much stronger ultrasonic probe. Hence, if only the particle size of single particles are required, when using an ultrasonic bath one can strictly speaking not view the results as being accurate.
7. Since ultrasonic bath pre-treatment cannot break up all agglomerates and aggregates, the subsequent particle size analysis results will not be accurate. A solution is to destroy all aggregates and agglomerates with chemical dissolution. Hence, if the wet samples is analysed directly afterwards, then ultrasonic treatment can be mild to minimise crystal damage and particle size modification. This is since all hard aggregates caused by cementing materials will have been removed; only possible softer agglomerates, bound by

van der Waals forces, will have to be broken up.

8. When breaking up the stronger *aggregates* is a prerequisite, and chemical dissolution is not used, then ultrasonic treatment must be applied – grinding in mortar and pestle can not effectively break up the stronger aggregates. However, then single particle break-up would probably occur.
9. To safeguard the comparability between different operators it is probably not necessary to conduct ultrasonic treatment at the same Watt value for the sonic vibrator. It is the *total amount* of ultrasonic energy *over time* that determines the complete break-up of agglomerates and aggregates (section 1.5.7.4). Hence for a specific sample the same cmp plateaus will most likely yield the same particle size distributions whether reached either at low ultrasonic energy over a longer time, or at higher ultrasonic energy over a shorter time (provided of course there is no single particle break-up).
10. The above error-results prove that differences in the intensity of grinding are the main determinant of the size of errors. But the intensity of grinding is impossible to duplicate. Because of this, even with light grinding the amount of hard aggregate break-up will be slightly different from one operator to the next. Hence, with samples where the break-up of *harder types of aggregates is important*, good comparability between several operators might be impossible to attain if grinding plus ultrasonic treatment are used above chemical dissolution.

Recommendations for further study:

1. To investigate whether complete hard *aggregate break-up* can be secured only with ultrasonic energy, it is suggested that the same experiments should be done again, but with a variable ultrasonic probe of a much higher energy than the ultrasonic bath. The results may indicate that light grinding prior to ultrasonic probe treatment can be omitted. This will solve the problem with comparability between different operators due to unavoidable differences in grinding intensity.
2. However, a high-energy ultrasonic probe might produce enough *single particle break-up* to noticeably undermine accuracy – especially at the smaller particle sizes. Therefore, to detect potential single particle break-up that could accompany ultrasonic probe treatments, the latter experiment needs to be augmented by an electron microscope study, aided by image analysis.
3. Determine whether low energy ultrasonic treatment for longer durations, will yield the

same cmp values for the larger particle sizes, but less single particle break-up (confirmed by SEM studies and lower cmp values at the smallest particle sizes).

4. Find the best combination between the mildest possible chemical dissolution and minimum ultrasonic energy and time, which will ensure the least modification of particle size. This should be conducted on as many soil types as possible, spanning a large variation in the degree of cementation. Try to find measurable parameters that can be used before ultrasonic treatment of every soil type to estimate the minimum chemical dissolution and ultrasonic time and energy nodded for it. Also, try to establish easily measurable parameters by which to establish when both pre-treatments can be terminated.
5. The possibility exists that the deflocculant polymers might undergo sono-chemical change during high-energy ultrasonic treatment (section 1.5.7.4). For this reason the supernatant solutions of each deflocculant type that were exposed to the longest ultrasonic treatments with a high intensity ultrasonic probe, must also be investigated for changes in molecular structure.
6. Test whether the varying the volume of the suspension and the bath water, different particle size distributions, solid concentration, and salt concentration, will notably alter the particle size distribution when conducting ultrasonic treatment the ultrasonic bath. This important to ensure comparability of results between different operators.
7. With the ultrasonic probe, find the correct magnitude of all the parameters to achieve optimum dispersion, without single particle break-up (section 1.5.7.4).
8. Fridman (1972) found that when by alternating mechanical break-up procedures with ultrasonic treatment, the de-aggregation efficiency of clay suspensions advanced dramatically. It is therefore suggested that an additional experiment should be conducted where vigorous mechanised shaking is combined with ultrasonic probe treatment.

4.1.3.2 The combined effect of kaolinite type, and soaking prior to sonication

The amorphous coating typically found on kaolinite surfaces becomes gel-like when exposed to water. Hence, when hard aggregates, cemented by these coatings, are soaked long enough in water, their bonding becomes weaker. Additionally, softer agglomerates are held together by van der Waals forces and salt-bridges. The latter, when caused by salts of low solubility like gypsum, might take long to dissolve. The duration of soaking prior to shaking and ultrasonic treatment should therefore influence the effectiveness of both to liberate single particles from aggregates and agglomerates.

It follows that if the specific aim is securing a particle size distribution of *single clay particles*, then increasing the soaking time will improve its accuracy. However, the soaking times of different samples must be of the same, and optimum, duration. Otherwise, reproducibility, repeatability, and accuracy of the succeeding analyses will not be achieved.

An experiment was planned to investigate the effect on the accuracy and repeatability of kaolinite samples when increased soaking foregoes ultrasonic treatment.

A second situation that has relevance to soaking is when the grinding-stage before ultrasonic treatment is omitted when soaking is conducted. The dry clay is only broken into lumps before weighing, and then ultrasonic treatment is commenced with directly thereafter. If grinding is not performed, the first de-aggregation step is omitted, which may reduce the accuracy of the particle size analysis following it (section 4.1.3.1). The magnitude of the effect of this approach on accuracy was also investigated.

4.1.3.2.1 Increased periods of soaking prior to ultrasonic treatment

The effect of soaking on accuracy and repeatability was actually illustrated already during the determination of optimum deflocculant concentration of Amazone coater in section 4.1.2.1. Those samples were soaked primarily in order to obtain repeatable results. The same samples that was re-soaked and re-sonicated until reproducible results were attained. As a result, the re-sonication could have masked the potential effect on aggregate break-up of soaking on its own.

An additional investigation was therefore necessary to ascertain whether soaking would modify particle size during the already mentioned practical set-up of a series of different samples analysed *over the period of a few days*. It was necessary to know whether diverse periods of soaking, followed by a single 3 min. sonication, would affect repeatability and reproducibility.

Materials and Methods:

All samples were lightly ground ahead of sample splitting in a spinning riffler. Six samples each of Serina filler, Dinkey coater and Amazone coater were suspended at its previously determined optimum Dispex concentration (see Tables 4.1.2.1.2 (a) – (d)). Dispex was chosen to disperse the suspension, since it proved itself as the best deflocculant. Additionally, it could contributed most to the break-up of agglomerates (see section 4.1.2.1).

Table 4.1.3.2.1.1. Determination of the effect of the duration of soaking preceding ultrasonic treatment

SOAKING TIME (DAYS)	Cum. Mass Percentage < 2 µm		
	SERINA FILLER (Dispex 1.2 %)	DINKEY COATER (Dispex 0.7 %)	AMAZONE COATER (Dispex 2.0 %)
0	59.0	82.5	98.0
1	59.0	83.0	99.5
2	59.0	82.5	99.0
3	59.0	83.0	98.0
4	59.0	83.5	99.5
5	59.0	83.0	99.0
Stdev. for soaking only:	0.0	0.4	0.6

All samples were suspended right at the start. Directly thereafter, a 3 min. ultrasonic treatment was administered to only one sample of each kaolinite type. These first samples were immediately analysed, without any foregoing soaking, but the other 5 samples of each kaolinite type was left soaking. Over the next 5 successive days one of the soaking samples of each kaolinite type was analysed. The cmps below 2 µm of each analysis is given in Table 4.1.3.2.1.1.

Results and Discussion:

The cmp values of Serina filler remained constant despite the increased soaking that preceded its ultrasonic treatment. However, both Dinkey coater and Amazone coater display a decrease in particle size due to increased soaking time preceding the ultrasonic treatment. After the full 5 days of soaking, Dinkey coater gave a 1% rise in cmp, and Amazone coater a 1.5% rise. Hence, if for these kaolinites the particle size analysis of *single particles* is required, then to secure accuracy with both kaolinite types they must be soaked before ultrasonic treatment.

Naturally, should all samples be made up at once and subsequently, with increasing soaking time, be analysed on successive days, then repeatability or reproducibility will likewise be reduced. This is confirmed by the higher standard deviation (stdev) of Dinkey and

Amazone as compared to that of Serina filler.

The results of Dinkey and Amazone furthermore disclose that 5 days are just enough to ensure their optimum aggregate break-up with ultrasonic treatment in an ultrasonic bath.

Conclusions:

1. Lightly ground Serina filler revealed that no soaking was necessary ahead of ultrasonic treatment to break up agglomerates and aggregates: it had the same result when analysed without soaking, as when soaked up to 5 days. Hence, when a long series of tests lasts up to 5 days, all Serina filler samples can be made up on the first day, and ultrasonicated just before analysis, without seriously affecting either of the accuracy, repeatability, and reproducibility.
2. With Dinkey coater and Amazone coater, though, the results of both prove that to improve accuracy they have to be soaked for at least one day. Thereafter, with increased soaking, neither accuracy, repeatability nor reproducibility is affected when ultrasonicated just before analysis.

4.1.3.2.2 Omitting soaking and grinding prior to ultrasonic treatment

The next step was to verify whether *grinding* before soaking and ultrasonic treatment was really necessary to ensure repeatability and reproducibility. By leaving out the grinding stage before weighing the samples would be beneficial, since it would reduce preparation time.

To extract maximum information, this test was carried without soaking. This could additionally establish whether soaking might cancel out the effect of omitting the grinding stage.

Materials and Methods:

For this experiment, two *un-ground* samples of each of Dinkey filler, Serina filler, and Amazone coater were made up with Dispex. The *first* un-ground sample of each kaolinite type was ultrasonicated for 3 min. directly after being suspended, and analysed down to 1 μm. Immediately thereafter the same sample was re-sonicated to a total ultrasonic time of 8 min. and re-analysed; finally it was re-sonicated again to a total ultrasonic time of 20 min., and the particle size analysis repeated.

Table 4.1.3.2.2.1. Difference in cmp between ultrasonic treatment in an ultrasonic bath executed directly after sample preparation, and ultrasonic treatment performed after 5 days of soaking.

(a) DINKEY FILLER (Dispex 0.1%), UNGROUND

ULTRASONIC TIME (min.)	CUMULATIVE MASS PERCENTAGE					
	ULTRASONIC TREATMENT DIRECTLY AFTER SAMPLE PREPARATION		ULTRASONIC TREATMENT AFTER 5 DAYS OF SOAKING			
	(CMP < 2μ)	(CMP < 1μ)	(CMP < 2μ)	Diff.	(CMP < 1μ)	Diff.
3.0	46.5	10.0	47.5	1.0	10.5	0.5
8.0	47.5	12.5	49.0	1.5	12.0	-0.5
20.0	50.0	13.0	49.0	-1.0	12.0	-1.0

(b) SERINA FILLER (Dispex 1.3%), UNGROUND

ULTRASONIC TIME (min.)	CUMULATIVE MASS PERCENTAGE					
	ULTRASONIC TREATMENT DIRECTLY AFTER SAMPLE PREPARATION		ULTRASONIC TREATMENT AFTER 5 DAYS OF SOAKING			
	(CMP < 2μ)	(CMP < 1μ)	(CMP < 2μ)	Diff.	(CMP < 1μ)	Diff.
3.0	56.0	42.0	57.0	1.0	42.5	0.5
8.0	56.5	42.5	57.5	1.0	43.5	1.0
20.0	57.0	43.0	58.5	1.5	44.0	1.0

(c) AMAZONE COATER (Dispex 1.3%), UNGROUND

ULTRASONIC TIME (min.)	CUMULATIVE MASS PERCENTAGE					
	ULTRASONIC TREATMENT DIRECTLY AFTER SAMPLE PREPARATION		ULTRASONIC TREATMENT AFTER 5 DAYS OF SOAKING			
	(CMP < 2μ)	(CMP < 1μ)	(CMP < 2μ)	Diff.	(CMP < 1μ)	Diff.
2.5	97.0	93.0	96.5	-0.5	94.5	1.5
5.0	99.0	97.5	99.0	0.0	98.0	0.5
20.0	99.5	98.5	99.5	0.0	98.5	0.0

The *second* un-ground sample of each kaolinite type was first soaked for 5 days. Afterwards the same regime of repeated ultrasonic treatments and analyses were re-applied. In all cases the cmps below both 2 μm and 1 μm were tabulated in Table 4.1.3.2.2.1 (a) to (c). To quantify the effect of soaking the difference between the cmp values of the soaked and un-soaked samples were calculated.

Results and Discussion:

The results in Table 4.1.3.2.1.1 (a) of the previous test revealed that when the samples were first *ground before soaking* and ultrasonic treatment, there was no increase in cmp for Serina filler – despite a soaking-time of up to 5 days. However, during the present test when Serina filler was soaked for the same period – but *without foregoing grinding* – it gave a 1% – 1.5% difference in cmp below 2 μm between soaked and un-soaked samples (Table 4.1.3.2.2.1 (b)). Besides that, there was also an increase in the difference in cmp between soaked and un-soaked samples as the ultrasonic time increased.

The results indicate that with *unground* Serina filler samples there is less ultrasonic break-up of agglomerates with soaking only, than when light grinding preceded soaking. This implies that, as with preliminary soaking, the preceding grinding likewise weakened aggregates, to assist in their later ultrasonic break-up. It is suspected that grinding creates micro-cracks in aggregates that enhance their ultrasonic break-up (section 1.5.7.4).

Furthermore, the solid particle clusters of Serina filler appears to contain a stronger aggregate type since even 20 min. of ultrasonic time was not enough to completely eradicate them. Should the cement be of a harder substance, this will make it more brittle. This will contribute to the formation of micro-cracks.

Contrary to Serina filler, when enlarging ultrasonic time with Amazone coater, there was a reduction in the cmp difference between soaked and un-soaked samples (Table 4.1.3.2.2.1 (c)). The cmp difference became zero somewhere between 5 and 20 min. of ultrasonic treatment. This indicates that a very long ultrasonic treatment of 20 min. was enough to destroy all the Amazone coater aggregates. In this way ultrasonic treatment eventually eradicated the effect of non-grinding.

The Amazone data furthermore imply that its aggregates are of a softer type than those of Serina filler. This is affirmed in the results of a previous section by the shorter ultrasonic times necessary for the un-ground and lightly ground samples of Amazone coater to reach their second cmp plateau (see Tables 4.1.3.1.1 (b) and (c) and Figures 4.1.3.1.1 (b), (c), and (d)). To

reach the first plateau took 7 min. for Amazone coater, as opposed to the 10 min. for Serina filler.

In the case of Dinkey filler there were unexpected results: at the two longer ultrasonic times there were a smaller increase in cmp with growth in ultrasonic time for the soaked sample as compared to the un-soaked sample (indicated by the negative differences) (Table 4.1.3.2.2.1 (a)). A possible explanation could be that when certain amorphous adhesives are present on kaolinite surfaces, then too long ultrasonic times can lead to re-agglomeration.

Conclusions:

1. The previous section pointed out that the effectiveness of agglomerate and aggregate break-up is determined by the magnitude of grinding energy and ultrasonic energy. This section's results in addition show that break-up is also determined by the duration of the preceding soaking. Hence to insure accuracy and reproducibility: at least overnight soaking must precede treatment in an ultrasonic bath.
2. For Serina filler, soaking combined with long ultrasonic treatment cannot be used to take the place of light grinding before soaking – even after soaking of up to 5 days. With Amazone coater, however, long enough ultrasonic treatment can replace grinding even with un-soaked samples. But this needs roughly 20 min. of ultrasonic treatment in an ultrasonic bath.

   On these grounds, to secure better accuracy, and to reduce treatment times in the *ultrasonic bath*, all unknown kaolinite samples need to be lightly ground in a mortar and pestle. Thereafter as standard procedure, they must be soaked overnight, and ultrasonicated once before analysis.
3. Kaolinites should not be treated in an ultrasonic bath for too long past the times needed to reach their second cmp plateaus. This may lead to re-agglomeration – hence accuracy will be sacrificed.
4. When applying reasonable ultrasonic times with Serina Filler and Dinkey filler one will not be analysing only single particles – hard aggregates will most likely still be present. This further implies that when the particle sizes of single clay particles are important, chemical dissolution should rather precede all particle size analyses.

Concluding remarks on ultrasonic treatment:

In order to attain accuracy and reproducibility for a specific operator – or to ensure comparability between different laboratories – a common ultrasonic time for use with all clay types cannot be prescribed in the standard procedure intended for all sedimentary methods. The reason is that agglomerate and aggregate strengths of every clay sample will be dissimilar, even for the relatively contaminant-free kaolinites examined above. Added to this, the frequencies and watt ratings of different ultrasonic baths and ultrasonic probes are also different, and the parameters controlling the break-up, especially with ultrasonic probes, are very diverse.

However, despite any combination of the parameters affecting ultrasonic break-up, when the same plateaus are reached for different samples of the same clay, then their particle size distributions will most likely be the same. Therefore, if the first and second plateaus are stipulated as the standard procedure for the break-up of agglomerates and hard aggregates, respectively, then results can safely be compared. In this way the minimum damage to single clay crystals, and the inaccuracy it will produce, will simultaneously be ensured.

If it is decided beforehand, though, that the contribution of *hard aggregates* can be *excluded* from the particle size analysis results, then it is recommended that an ultrasonic time of 1 min. past the *first plateau* should be used as the standard with ultrasonic baths. In this way only the weaker agglomerates, which is bound by van der Waals bonds, will be eliminated.

Should, on the other hand, the particle size analysis of only single particles be the aim, then stronger aggregates should rather be eliminated by dissolution treatment, and not by intense or long ultrasonic treatment. This will safeguard accuracy since single particles will not be broken up while the stronger aggregates are destroyed. It must be still followed by ultrasonic treatment of 1 min. past the first plateau, since weaker agglomerates need to be broken up. They will most likely form after drying and weighing following dissolution, or due to strong enough van der Waals bonds forming during flocculation accompanying dissolution treatment, as well as during deposition under centrifugal force. This will additionally reduce ultrasonic time.

Suggestions for further study:

The above explanation for the formation of the two plateaus (first the break-up of weaker agglomerates and/or flocks, followed by stronger aggregates with no break-up of individual kaolinite particles) is not proved by the data on its own. The explanation of the plateaus can

only be regarded as feasible speculative suggestions for some of the observed patterns in the data. The same is true of the explanations offered for the preliminary soaking of samples.

In order to clarify the mechanisms behind the observed patterns, an additional study is suggested where the grinding, soaking, and ultrasonic treatment tests of all the kaolinites of section 4.1.3.1 be performed again. Then, after each ultrasonic step, the suspensions should be studied with both the light and electron microscopes. This is to directly observe whether the fining of samples with grinding, soaking and/or increased ultrasonic time is due to one or more of the deflocculation, de-agglomeration or de-aggregation mechanisms. Potential single particle breakage must also be investigated. Such a study will reveal at what ultrasonic duration does the break-up of which one of these three types of particle assemblies start to become a factor. For this purpose, the light microscope dark-field illumination must be used, to be able to explicitly distinguish between different single particles. Furthermore, by carefully increasing the pressure on the cover glass will enable the distinguishing between flocks, stronger aggregates, and weaker agglomerates.

When using either the TEM or SEM the following approach can be used to distinguish between agglomerates and/or aggregates and flocks. On the TEM and SEM sample grids solid particle assemblies, such as agglomerates and aggregates, will have particles orientated in all directions. In contrast, when sample suspensions are dried on TEM or SEM sample grids, then the separate particles making up the original flocks will all deposit horizontally upon each other. The SEM will furthermore also yield information on conceivable damage to crystal surfaces caused by ultrasonic energy, rotational breakage during grinding, as well as on splitting along {001} cleavage planes. In its natural form, Serina samples already have irregular and often broken crystal forms. It therefore cannot be used with an electron microscope to demonstrate rotational breakage. However, Dinkey and Amazone have near perfect crystal forms, and can therefore be used to illustrate rotational breakage, since it will cause irregular crystal edges. The shadowing technique can furthermore be applied to establish the thickness of kaolinite platelets (Środoń *et al.*, 1992). Combined with image analysis this can reveal the magnitude of possible splitting along {001} cleavage planes due to both ultrasonic treatment and grinding.

Information that is more useful will be acquired from this additional study if the entire particle size distribution is noted down (not only the cmp smaller than 2 μm and 1 μm as in the above experiments). This can reveal which larger particle sizes have broken up to enrich which smaller particle sizes. It may also more clearly distinguish between de-agglomeration, de-aggregation, and single particle break-up.

4.1.3.3 The influence of stirring on the efficiency of ultrasonic treatment

The ASTM standard C958 (1981) prescribes that a 5 min. ultrasonic treatment, with frequent stirring, is applied to alumina or quartz particles prior to all sedimentary methods of particle size analysis.

A good reason for stirring during ultrasonic treatment might be that the top part of the suspension initially experiences more cavitation (Walmsley and Williams, 1991). But later, cavitation at the bottom will dominate due to increased liquid pressure (Fridman, 1972). Therefore, at different stages, unequal fining will take place in the top and bottom parts. However, stirring will allow all parts of the suspension to be affected equally, causing more effective break-up of agglomerates and aggregates.

Experience also shows that many of the largest particles deposits on the bottom before the 3 min. ultrasonic treatment is completed. Cavitation in such tightly packed sediment might not be possible, restraining agglomerate break-up. To prevent this, all particles should be kept in suspension during ultrasonic treatment.

For these reasons the need, or not, to stir kaolinite samples while using an ultrasonic bath, was also investigated.

Materials and Methods:

To investigate the effect of stirring during ultrasonic treatment, 12 different samples of Serina filler 2 were made up at a 1.2% Dispex concentration. Serina filler was chosen because it apparently has the hardest aggregates of all.

Directly after being made up, and just before analysis, the first 3 samples were given a 3 min. ultrasonic treatment in the ultrasonic bath. Directly afterwards, each one of these samples was analysed with the Sedigraph, and their cmps below 2 μm were recorded in Table 4.1.3.3.1. During sonication, the suspensions were still in the plastic sample storage bottles in which all samples are made up. The bottles were only shaken for the standard one minute to re-suspend the sediment from the bottom. For the first runs, ultrasonic treatment was conducted without any stirring to obtain a standard against which to test the effect of stirring during sonication.

The second 3 samples were again shaken for 1 min., but this time it was poured in a 100 ml Pyrex beaker to allow stirring in the ultrasonic bath. For this purpose, a stirrer equipped with a PVC propeller, and adjusted to its lowest setting, was used.

A third set of 3 samples was similarly ultrasonicated for 3 min., but at a medium stirrer speed setting of 3. A last set of three samples was investigated in the same manner, but at the fast stir speed setting of 6. The 9 stirred samples were also analysed directly after ultrasonic treatment, and their cmps below 2 µm recorded (Table 4.1.3.3.1).

Table 4.1.3.3.1. Determination of the effect of stirring during ultrasonic treatment in an ultrasonic bath.

SERINA (Dispex 1.2 %).

SAMPLE NUMBER	PLASTIC BOTTLE NO STIRRING	 Cum. Mass % < 2 µ
1	-	59.5
2	-	59.5
3	-	59.5
SAMPLE NUMBER	**100 ml PYREX BEAKER STIR SPEED**	** Cum. Mass % < 2 µ**
4	1	59.5
5		59.5
6		59.5
7	3	59.5
8		59.5
9		59.5
10	6	59.5
11		59.5
12		59.5

Results and Discussion:

The results show that all the stirred samples gave the same results as the unstirred ones. Evidently, stirring had no effect on the effectiveness of ultrasonic treatment.

Conclusions:

In the specific ultrasonic bath used during this study, the samples can be ultrasonicated within their plastic containers without being stirred.

When ultrasonic treatment is performed in an ultrasonic bath, neither the unlike dimensions between storage bottles and the glass container, nor their different materials

(plastic and glass) have any effect

Since ultrasonic treatment was always preceded here by 1 min. of shaking to re-suspend sediment from the bottom, it was duplicated during all analyses of the rest of this study.

Recommendations for further study:

1. It is suggested that this experiment be repeated to also test the effect of stirring during ultrasonic treatment on all the other types of kaolinites. Differences in their agglomerate and aggregate strengths may have an effect.
2. Three additional samples, which are not shaken before ultrasonic treatment, can be added to this test. This is to learn whether it would make any difference when the larger particle fraction – that probably contains most of the agglomerates and aggregates – are still deposited at the bottom during ultrasonic treatment. The reason for including this test is to show what might happen when the operator forgets to shake the sample before sonication.
3. A second set of 16 samples should additionally be examined in the same way, but after 5 days of soaking.
4. This test should as a whole be duplicated with an ultrasonic probe while varying all the additional factors mentioned in the introduction of section that can also play a role in the efficiency of ultrasonic break-up.

4.2 TESTING THE INFLUENCE OF THE PHYSICAL AND CHEMICAL PROPERTIES OF CLAY SUSPENSIONS ON ACCURACY AND REPRODUCIBILITY

Under discussion in this part are the effects on accuracy and reproducibility of the parameters associated with the physical properties of the suspension. They can be subdivided into two types:

1. The parameters connected only to the physical and chemical properties of the suspension liquid. The liquid in which the clay is suspended is defined here as the suspension liquid. With clay size analyses, the suspension liquid is always distilled water plus a deflocculant. Two aspects will be discussed:
    - the effect on accuracy when the density and viscosity of distilled water are used to calculate the scan rate, instead of that of the suspension liquid.
    - the effect of using only distilled water to adjust the 0% setting, instead of using

the suspension liquid.

2. The parameters related to the physical properties of clay suspensions as a whole, which involves:

   - the consequence of the potential hydrolysis of deflocculants produced by the highly active clay surfaces
   - the impact hindered settling at different solid concentrations can have on accuracy and reproducibility.

4.2.1 The influence of deflocculants on the physical properties of the suspension liquid

During all of the sedimentary methods the density and viscosity of the suspension liquid is of great importance. Accurate densities and the viscosities at different temperatures are essential to correctly calculate particle size. With the Sedigraph it is needed to calculate the sample cell scan rate (Eq. 1.4.2.2), which is in turn used in accurately registering its particle size distribution (section 4.2.1).

Although the suspension liquid also contains a deflocculant, the density and viscosity of only distilled water are used to calculate the cell scan rate for Sedigraph analysis. A question that can be asked is: when this practice is followed, will the deflocculant polymers alter the suspension liquid properties enough to induce inaccurate results? Therefore, an experiment was conceived to calculate the cmp error if the density and viscosity of water is used in scan rate calculations instead of those of the actual suspension liquid.

As first steps the experimentally determined differences between density and viscosity of the suspension liquids and that of water was determined. To accomplish this, the densities of the suspension liquids of each deflocculant type were established by means of a liquid pycnometer. Thereafter the suspension liquid viscosities were determined by means of an Obolt viscometer. From these the errors in scan rate were calculated. Lastly, using regression analysis of experimental results the errors in scan rate (should the density and viscosity of distilled water be used to calculate it) were relayed to errors in cmp.

Different kaolinite types have unlike optimum deflocculant concentrations, and different deflocculants have unlike molecular sizes. Both aspects would therefore lead to diverse amounts of deflocculant in the suspension liquid for each kaolinite/deflocculant combination. Moreover, the different kaolinite types have dissimilar total surface areas. Each kaolinite type will therefore remove different amounts of dispersant from the solution through adsorption to

its particle surfaces. Therefore, even in cases where the same amount of a deflocculant was added to each of the kaolinite types, the variations in their total surface areas will cause different densities and viscosities for their respective suspension liquids.

Therefore, to be able to study suspension liquids representative of each of the kaolinite types used during this study, the next steps were taken:

First, each kaolinite type was suspended with each deflocculant at its optimum concentration (section 4.1.2.1). Next, suspension liquids were obtained by centrifuging the suspensions in an ultracentrifuge until the supernatant liquid was clear of suspended clay particles. Since those deflocculant adsorbed on clay surfaces was removed, the supernatants now had the same deflocculant concentrations as the real suspension liquids. The supernatants of every kaolinite suspension could therefore be used to determine the actual densities and viscosities encountered by their settling particles.

The densities of the supernatant suspension liquids had to be established first, since they were needed to convert experimental viscometer results into viscosity values.

4.2.1.1 Experimental determination of the densities of suspension liquids

The first step in the density determinations was to calibrate the volumes of the liquid pycnometers used for this purpose. To improve both the accuracy and the ease of pycnometric density determinations, a novel method was developed during this study. It will be described directly below.

4.2.1.1.1 Volume calibration of the liquid pycnometers

With the new method, the first step was to calibrate the volumes of a few pycnometers over the normal range of temperature increase expected for a room without temperature control. Using the values of volume against temperature, a regression formula was acquired with Quattro Pro software[12] for each pycnometer. Using these formulas, the pycnometer volumes could thereafter be calculated at any room temperature.

With the standard method, a number of pycnometer volume determinations are first performed at the same temperature (ISO 758:1976[13]). From these an average pycnometer volume is calculated. Thus, the pycnometer is calibrated for only one specific temperature.

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[12] *Quattro Pro spread sheet software for Windows, Borland International Inc. (1993).*

[13] *ISO 758:1976 Liquid chemical products for industrial use -- Determination of density at 20 degrees C*

Hence, all density determinations must thereafter be conducted at only that specific temperature. The standard method therefore requires precise and elaborate temperature control.

In contrast, with the novel method the pycnometer volumes were plotted at several temperatures, chosen over the whole range of room temperature variation. This gave an average change in pycnometer volume with change in temperature. It replaced the single average pycnometer volume at only one fixed temperature of the standard method. This so-called 'average change in pycnometer volume' was obtained by calculating a regression formula of the straight line best fitting the volume and temperature data (Table 4.2.1.1.1.2 (a) - (e) and Figures 4.2.1.1.1.1 (a) - (e)).

Therefore, with the novel method the need to keep the temperature of the pycnometer at precisely the same temperature as its original volume calibration during subsequent density determinations was done away with. The density determinations could now accurately be carried out at any temperature within the normal range of room temperature variation.

Using a regression formula for volume against temperature is not only easier, faster and cheaper; it additionally provides more accurate pycnometer volume determinations than the standard method. Accuracy is improved because the density at every 0.1 °C change in temperature can now be calculated. The new approach can both be followed during the volume determinations of the initial calibration stage, as well as during the later determination of the unknown densities of other liquids. On the other hand, during the initial calibration stage of the standard method the controlled temperature frequently differs with more than 0.1 °C from the chosen single temperature. As a consequence, the initial pycnometer volume will already be calibrated less accurately. This inaccurate volume is then used during the subsequent determinations of unknown densities of other liquids. Here, again, the same temperature error will be reproduced. Densities acquired with the standard method will therefore be doubly inaccurate.

With the novel method the only factors determining accuracy are the continued cleanness of the pycnometers to keep its weight constant, the accuracy of the thermometer, the homogeneity of temperature in the pycnometer liquid when registering the temperature, and the accuracy of weighing. All of these prerequisites can be attained with relative ease and precision.

Materials and Methods:

To obtain the required range of temperatures, the increase in room temperature during a summer day was utilised. This gave a temperature rise ranging from 19 °C to 28 °C. The liquid used for the volume calibration was triple distilled water, purified further by means of an ion exchange system.

During the volume calibrations, the pycnometer water temperature was determined with a standard mercury thermometer to an accuracy of 0.1 °C. However, to calculate the volumes to that accuracy, the density values of pure water from the Handbook of Chemistry & Physics (Weast, 1980) could not be used as-is. These densities are supplied in large temperature steps of 1 °C. To solve this, the Handbook of Chemistry & Physics density values were used to first obtain a regression formula for density against temperature. Water densities were then calculated at every 0.1 °C step over the temperature range expected during the experiment. The formula, the density values for pure water (Handbook of Chemistry & Physics), and densities for pure water at every 0.1 °C temperature step are given in Table 4.2.1.1.1.1.

To affirm the accuracy of the regression formula, the difference between the calculated and handbook densities were calculated as well (Table 4.2.1.1.1.1). The maximum difference between the calculated density values and the actual handbook densities was only -0.0000005 g/cm^3. This represents a maximum error in the calculated density values of only –0.00005%, corresponding to a temperature error in the vicinity of 0.012 °C. The regression formula was therefore precise enough to be used with the standard mercury thermometer that was accurate to 0.02 °C.

The first step in calibrating a pycnometer was to fill it to the brim with distilled water. The distribution of heat within the pycnometer was homogenised by stirring it with the standard mercury thermometer, until a constant water temperature was registered right through. Immediately thereafter, the glass stopper was inserted. Care was taken not to enclose air bubbles when inserting the stopper. This assured an accurate volume determination.

By holding the pycnometer by the neck with a paper towel, any water spilling over when inserting the stopper was intercepted. This 'paper clamp' also precluded a rise in pycnometer temperature due to direct finger contact. The filled pycnometer was placed on the scale pan, and the mass recorded along with the temperature of weighing. With the novel method, a further improvement on accuracy was made by quickly wiping dry the glass stopper hole and the fitting between stopper and pycnometer neck when already on the scale pan.

Table 4.2.1.1.1.1. Difference between actual and calculated density values of pure water between 0 ° to 45 °C.

The calculated density of pure water was secured by means of the following Multiple Regression Model fitted to the actual density values of pure water with temperatures in steps of 1°C (from Weast, 1980) using Stepwise Variable Selection with Statgraph statistical software:

$$\text{Calculated Density} = 6.249046 \times 10^{-24} \times T^{11} - 8.78038 \times 10^{-14} \times T^{6} + 1.570443 \times 10^{-11} \times T^{5} - 1.456911 \times 10^{-9} \times T^{4} + 1.050836 \times 10^{-7} \times T^{3} - 9.119179 \times 10^{-6} \times T^{2} + 0.000068 \times T + 0.999843$$

CHOSEN TEMP. (°C)	CALCULATED DENSITY (g/cc)	ACTUAL DENSITY (g/cc) (H.B. of Chemistry and Physics values)	DENSITY DIFFERENCE (ACTUAL - CALCULATED) (g/cc)
0	0.9998430	0.9998425	-0.0000005
1	0.9999020	0.9999015	-0.0000005
2	0.9999433	0.9999429	-0.0000004
3	0.9999677	0.9999672	-0.0000005
4	0.9999755	0.9999750	-0.0000005
5	0.9999673	0.9999668	-0.0000005
6	0.9999436	0.9999432	-0.0000004
7	0.9999050	0.9999045	-0.0000005
8	0.9998517	0.9998512	-0.0000005
9	0.9997843	0.9997838	-0.0000005
10	0.9997031	0.9997026	-0.0000005
11	0.9996085	0.9996081	-0.0000004
12	0.9995009	0.9995004	-0.0000005
13	0.9993805	0.9993801	-0.0000004
14	0.9992478	0.9992474	-0.0000004
15	0.9991030	0.9991026	-0.0000004
16	0.9989464	0.9989460	-0.0000004
17	0.9987783	0.9987779	-0.0000004
18	0.9985990	0.9985986	-0.0000004
19	0.9984086	0.9984082	-0.0000004
20	0.9982075	0.9982071	-0.0000004
21	0.9979959	0.9979955	-0.0000004
22	0.9977739	0.9977735	-0.0000004
23	0.9975419	0.9975415	-0.0000004
24	0.9972999	0.9972995	-0.0000004
25	0.9970483	0.9970479	-0.0000004
26	0.9967871	0.9967867	-0.0000004
27	0.9965166	0.9965162	-0.0000004
28	0.9962369	0.9962365	-0.0000004
29	0.9959482	0.9959478	-0.0000004
30	0.9956506	0.9956502	-0.0000004
31	0.9953444	0.9953440	-0.0000004
32	0.9950296	0.9950292	-0.0000004
33	0.9947063	0.9947060	-0.0000003
34	0.9943748	0.9943745	-0.0000003
35	0.9940352	0.9940349	-0.0000003
36	0.9936876	0.9936872	-0.0000004
37	0.9933320	0.9933316	-0.0000004
38	0.9929687	0.9929683	-0.0000004
39	0.9925976	0.9925973	-0.0000003
40	0.9922191	0.9922187	-0.0000004
41	0.9918331	0.9918327	-0.0000004
42	0.9914397	0.9914394	-0.0000003
43	0.9910391	0.9910388	-0.0000003
44	0.9906313	0.9906310	-0.0000003
45	0.9902165	0.9902162	-0.0000003

Max. value for density difference : - 0.0000005 (g/cc)

Table 4.2.1.1.1.2. Comparing the effect of two approaches to weighing on the accuracy and reproducibility of pycnometer density determinations

(a) Weighing directly after wiping the neck and stopper hole, while already on the scale pan

TEMPERATURE MEASURED IN PYCNOMETER AT WEIGHING (°C)	MASS OF PYCNOMETER FILLED WITH WATER (g)	MASS OF WATER IN PYCNOMETER (g) (MASS FILLED - MASS EMPTY)	EXPERIMENTAL VOLUME OF PYCNOMETER (cc) MASS WATER / CALC. DENSITY WATER	VOLUME OF PYCNOMETER CALCULATED BY MEANS OF LINEAR REGRESSION (ml)
20.2	40.5223	24.2864	24.3310	24.3311
20.3	40.5222	24.2863	24.3314	24.3312
22.0	40.5146	24.2787	24.3329	24.3328
22.1	40.5143	24.2784	24.3331	24.3329
23.4	40.5079	24.2720	24.3341	24.3342
23.6	40.5069	24.2710	24.3343	24.3344
24.7	40.5010	24.2651	24.3351	24.3354
24.8	40.5007	24.2648	24.3354	24.3355
25.6	40.4963	24.2604	24.3360	24.3363
25.7	40.4955	24.2596	24.3359	24.3364
26.3	40.4931	24.2572	24.3373	24.3370
26.6	40.4911	24.2552	24.3373	24.3373
26.9	40.4898	24.2539	24.3380	24.3375
27.2	40.4877	24.2518	24.3379	24.3378

Fig. 4.2.1.1.1 (a)

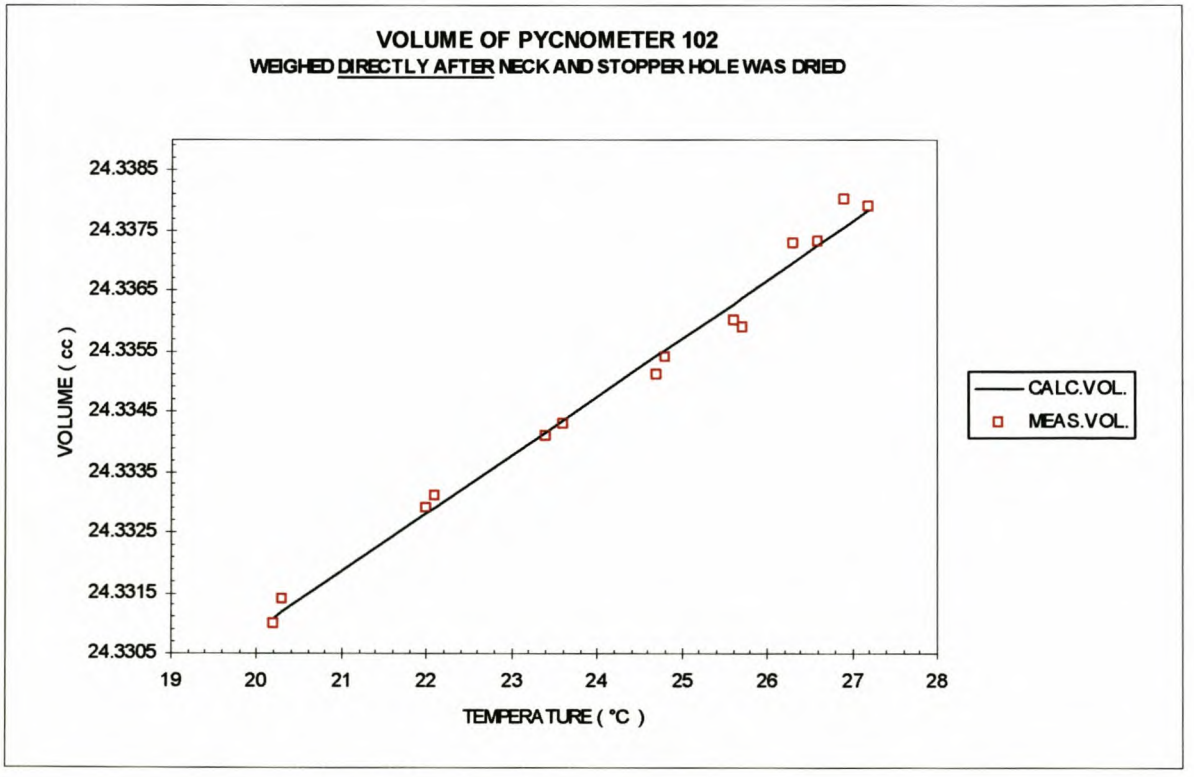


Table 4.2.1.1.1.2 (b)

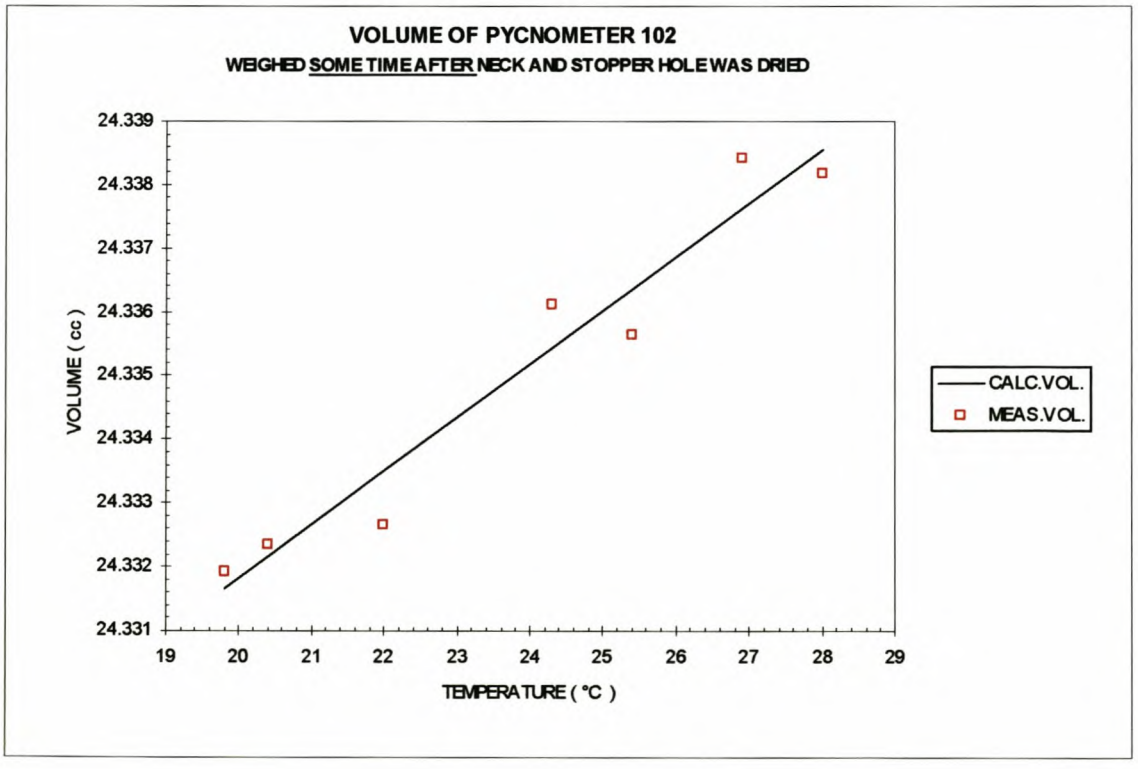
Weighing when some time had ellapsed after wiping the neck and stopper hole dry

The Calculated Volume was determined by means of the following formula obtained by Linear Regression of the Experimental Volume values using Quattro Pro software :

Calculated Volume = 24.315024 + (0.0008400822 x Measured Temperature)

TEMPERATURE MEASURED IN PYCNOMETER AT WEIGHING (°C)	MASS OF PYCNOMETER FILLED WITH WATER (g)	MASS OF WATER IN PYCNOMETER (g) (MASS FILLED - MASS EMPTY)	EXPERIMENTAL VOLUME OF PYCNOMETER (cc) MASS WATER / CALC. DENSITY WATER	VOLUME OF PYCNOMETER CALCULATED BY MEANS OF LINEAR REGRESSION (cc)
19.8	40.5252	24.2893	24.3319	24.3317
20.4	40.5226	24.2867	24.3323	24.3322
22.0	40.5144	24.2785	24.3327	24.3335
24.3	40.5045	24.2686	24.3361	24.3354
25.4	40.4972	24.2613	24.3356	24.3364
26.9	40.4902	24.2543	24.3384	24.3376
28.0	40.4825	24.2466	24.3382	24.3385

Fig. 4.2.1.1.1 (b)



As the temperature rose during the rest of the day, this procedure was repeated a number of times, at increasingly higher temperatures. The pycnometer volumes were calculated (Table 4.2.1.1.1.2 (a)), and are visually presented in Fig. 4.2.1.1.1.2 (a). To show the improvement in accuracy and reproducibility brought by wiping on the scale pan, the volumes determined when prior wiping was not done in this manner are also presented in Table 4.2.1.1.1.2 (b), and Fig. 4.2.1.1.1.2 (b).

To ensure accurate weighing, any movement of air must be avoided in the scale pan compartment (Weast, 1980). To secure this the scale pan, the weighed object, and the air inside the scale pan compartment need to be at the same temperature. For this reason the scale, supernatant liquids, and pycnometers were placed beforehand in the same room, to stabilise to the same temperature. When not busy weighing, the scale compartment was left open to allow it to keep pace with the temperature change in the room.

Results and Discussion:

When weighing the pycnometer before placing it on the scale pan, it had a correlation coefficient of 0.944267. However, weighing speedily by wiping the pycnometer on the scale pan, the volume change with changing temperature gave a better correlation coefficient of 0.987229 (also compare Figures 4.2.1.1.1.2 (a) and (b). This indicates that faster wiping and weighing during pycnometer volume determinations lead to an improvement in accuracy and reproducibility.

When a filled, stoppered, and dried-off pycnometer is placed on the scale pan, its mass continually decreases for as long as being left like that. This can only be caused by evaporation from the stopper-fitting, as well as from the stopper-hole. With this in mind the explanation for the above improvement in the correlation coefficient when wiping is done on the scale pan is as follows:

Wiping the neck and stopper-hole on the scale pan *directly* before weighing will provide less time for evaporation. In addition, the intervals between wiping and weighing could be kept shorter and more constant, than when wiping the pycnometer on the table, followed by careful placement on the scale pan. Hence, variations in the amount of evaporation of water through the stopper-hole and stopper-fitting were reduced, lowering the fluctuations in weight loss, and therefore improving both accuracy and reproducibility.

4.2.1.1.2 Determining the densities of suspension liquids for all the kaolinite/deflocculant combinations

In order to determine the densities of the suspension liquids of all the kaolinite/deflocculant combinations, the suspended clay first had to be completely removed first. Thereafter the same methodology was used as with the volume calibration of the pycnometers.

Materials and Methods:

Each of 9 kaolinite/deflocculant combinations (*i.e.* Serina filler 2, Dinkey coater (D_{max} 50 µm) and Amazone coater in combination with Calgon, Dispex and Floccotan) was made up at their optimum deflocculant concentrations (see Table 4.1.2.1). These three kaolinite types were used since they represent a diversity in textures ranging from a finer particle size distribution (Amazone coater), through a medium one (Dinkey coater - D_{max} 50 µm), to a coarser one (Serina filler). This was to ensure that both the greatest and smallest amounts of removal of deflocculant through adsorption on clay surfaces were illustrated. Hereby was made certain that the suspension liquid with potentially the largest deviation in density above that of pure water (Serina Filler 2) were represented, along with the one with the least deviation in density (Amazone filler). The density of the supernatant liquid of the intermediate suspension (Dinkey coater (D_{max} 50 µm)) was added in order to establish if there is a pattern due to a possible diversity in the deflocculant adsorption of different kaolinite types.

Most of the suspended clay of each sample was removed in a centrifuge. The centrifuge head with inclined centrifuge tubes was chosen to speed up sedimentation. Centrifugation was conducted at 12500 rpm for 30 min. The supernatant liquid was afterwards decanted into smaller ultracentrifuge tubes, and centrifuged again for 45 min. at 25000 rpm, to ensure that the last of the ultra-small particles still in suspension was removed. Careful removal of the tubes, and fast decantation, prevented re-suspension of deposited clay was from the bottom during decantation of the clean supernatant liquids.

Using one pycnometer, the densities of the supernatant liquids of each kaolinite/deflocculant combination were determined. To acquire average densities, at least 6 volume determinations were performed for each supernatant liquid. The same procedure was followed here for pycnometer volume determinations as described in the previous section 4.2.1.1.1.

At this stage, accuracy and reproducibility were further improved by keeping weight loss

due to evaporation during weighing to a minimum. This was done by preventing continuous up-welling of water through the stopper-hole after being wiped dry. Such water covered the top surface of the stopper, providing a much bigger evaporation surface area than that of the capillary meniscus. Continued up-welling was caused when, with the rise in the room temperature, the thin glass of an empty pycnometer warmed up faster than the supernatant liquids. The pycnometer volume therefore decreased when a slightly colder supernatant liquid was added to the warmer pycnometer, pushing water out through the capillary. To prevent this: each time before the filled pycnometer was stoppered and dried, it was covered in a paper towel, and warmed to room temperature by covering it with both hands. The paper towel prevented finger-fat and perspiration from changing the mass of the pycnometer.

To acquire the mass of the suspension liquid, the pre-weighed empty mass of the pycnometer was subtracted from the mass when filled. The previously determined regression formula (Table 4.2.1.1.1.2 (a)) was used to convert the supernatant liquid mass to volume at the temperature of weighing. By using the mass and volume of the suspension liquid, its density could be calculated (Tables 4.2.1.1.2.1 (a) - (i))

The density of pure water, at the same temperature as each separate supernatant density determination, were transferred from Table 4.1.1 to Tables 4.2.1.1.2.1 (a) – (i). The differences between the densities of the supernatant liquids and that of pure water were calculated, and their averages obtained. These density differences are the errors in density if the density of pure water is used in cell scan rate determinations, instead of that of the suspension liquid.

Finally, the percentages by which the density of water differs from that of the true densities of the suspension liquids were computed in the "Percentage Error in Density" columns, Tables 4.2.1.1.2.1 (a) – (i).

Results and Discussion:

Of all suspension liquids, those of Amazone coater generally display the largest density differences with that of pure water, followed by those of Serina filler 2. Those of Dinkey filler differed least from that of pure water. But, surprisingly, when deflocculated with Calgon or Dispex, Dinkey filler had supernatant densities slightly lower than that of water.

Table 4.2.1.1.2.1. Determination of the difference between the density of water and that of the supernatent liquids of Dinkey, Serina and Amazone suspensions at their optimum deflocculant concentrations for Calgon, Dispex and Floccotan.

The volume of the pycnometer was calculated with the following formula: Calculated Volume = Temp. x 0.000962574 + 24.3116. This formula was obtained by means of Linear Regression of the experimental volume values, by using Quattro Pro software.

The density of pure water for temperatures accurate to 0.1°C, was calculated by means of the following Multiple Regression Model: Calculated Density = $6.249046 \times 10^{-24} \times T11 - 8.78038 \times 10^{-14} \times T^6 + 1.570443 \times 10^{-11} \times T^5 - 1.456911 \times 10^{-9} \times T^4 + 1.050836 \times 10^{-7} \times T^3 - 9.119179 \times 10^{6} \times T^2 + 0.000068 \times T + 0.999843$. This formula was obtained by fitting the actual density values for temperatures accurate to 1°C (Weast (1980) using Stepwise Variable Selection with Statgraph statistical software.

(a) CALGON 0.1 % (DINKEY FILLER; Dmax 50 µm)

MASS OF FILLED PYKNOMETER (g)	MASS OF SUPERNATANT (g) (Filled - Empty)	TEMPERATURE MEASURED AT WEIGHING (°C)	CALCULATED VOLUME OF PYKNOMETER (g)	DENSITY OF SUPERNATANT (g/cc) Mass dispersant / Vol. of pyknometer	CALCULATED DENSITY OF WATER AT SAME TEMPERATURE AS DURING WEIGHING THE SUPERNATANT (g/cc)	ERROR IN DENSITY (g/cc) (Dispersant - Water)	PERCENTAGE ERROR IN DENSITY (%)
40.5126	24.2765	21.8	24.3326	0.997695	0.997819	-0.000124	-0.012432936
40.5105	24.2744	22.1	24.3329	0.997597	0.997751	-0.000154	-0.015459909
40.5101	24.2740	22.1	24.3329	0.997581	0.997751	-0.000171	-0.017108018
40.5111	24.2750	21.8	24.3326	0.997633	0.997819	-0.000186	-0.018612901
40.5114	24.2753	21.8	24.3326	0.997646	0.997819	-0.000173	-0.017376847
40.5142	24.2781	21.4	24.3322	0.997777	0.997908	-0.000132	-0.013198271
					Average:	-0.000157	-0.015698147

(b) CALGON 0.6 % (SERINA FILLER 2)

MASS OF FILLED PYKNOMETER (g)	MASS OF SUPERNATANT (g) (Filled - Empty)	TEMPERATURE MEASURED AT WEIGHING (°C)	CALCULATED VOLUME OF PYKNOMETER (g)	DENSITY OF SUPERNATANT (g/cc) Mass dispersant / Vol. of pyknometer	CALCULATED DENSITY OF WATER AT SAME TEMPERATURE AS DURING WEIGHING THE SUPERNATANT (g/cc)	ERROR IN DENSITY (g/cc) (Dispersant - Water)	PERCENTAGE ERROR IN DENSITY (%)
40.5263	24.2902	21.3	24.3321	0.998278	0.997930	0.000348	0.034810034
40.5178	24.2817	22.7	24.3335	0.997873	0.997613	0.000261	0.026128219
40.5198	24.2837	22.2	24.3330	0.997975	0.997728	0.000247	0.024737916
40.5210	24.2849	22.5	24.3333	0.998013	0.997659	0.000354	0.035422095
40.5246	24.2885	21.6	24.3324	0.998196	0.997864	0.000332	0.033282211
40.5225	24.2864	21.6	24.3324	0.998110	0.997864	0.000246	0.024638274
					Average:	0.000298	0.029836458

(c) CALGON 1.0 % (AMAZONE COATER)

MASS OF FILLED PYKNOMETER (g)	MASS OF SUPERNATANT (g) (Filled - Empty)	TEMPERATURE MEASURED AT WEIGHING (°C)	CALCULATED VOLUME OF PYKNOMETER (g)	DENSITY OF SUPERNATANT (g/cc) Mass dispersant / Vol. of pyknometer	CALCULATED DENSITY OF WATER AT SAME TEMPERATURE AS DURING WEIGHING THE SUPERNATANT (g/cc)	ERROR IN DENSITY (g/cc) (Dispersant - Water)	PERCENTAGE ERROR IN DENSITY (%)
40.5322	24.2961	21.2	24.3320	0.998524	0.997952	0.000572	0.057283435
40.5293	24.2932	21.8	24.3326	0.998381	0.997819	0.000562	0.056319128
40.5275	24.2914	22.2	24.3330	0.998292	0.997728	0.000563	0.056428536
40.5264	24.2903	22.4	24.3332	0.998239	0.997682	0.000556	0.055720994
40.5306	24.2945	21.5	24.3323	0.998447	0.997886	0.000561	0.056138165
40.5300	24.2939	21.7	24.3325	0.998414	0.997842	0.000573	**0.057345653**
					Average:	**0.000564**	**0.056539318**

Tables 4.2.1.1.2.1 continued: (d) – (g)

(d) DISPEX 0.1 % (DINKEY FILLER; Dmax 50 µm)

MASS OF FILLED PYKNOMETER (g)	MASS OF SUPERNATANT (g) (Filled - Empty)	TEMPERATURE MEASURED AT WEIGHING (°C)	CALCULATED VOLUME OF PYKNOMETER (g)	DENSITY OF SUPERNATANT (g/cc) Mass dispersant / Vol. of pyknometer	CALCULATED DENSITY OF WATER AT SAME TEMPERATURE AS DURING WEIGHING THE SUPERNATANT (g/cc)	ERROR IN DENSITY (g/cc) (Dispersant - Water)	PERCENTAGE ERROR IN DENSITY (%)
40.5149	24.2788	21.9	24.3327	0.997786	0.997797	-0.000011	**-0.001093904**
40.5158	24.2797	21.6	24.3324	0.997835	0.997864	-0.000029	-0.002949996
40.5157	24.2796	21.7	24.3325	0.997826	0.997842	-0.000015	-0.001517754
40.5151	24.2790	21.9	24.3327	0.997794	0.997797	-0.000003	-0.000270138
40.5111	24.2750	22.7	24.3335	0.997598	0.997613	-0.000015	-0.001464982
40.5151	24.2790	21.8	24.3326	0.997798	0.997819	-0.000021	-0.002134691
					Average:	**-0.000016**	**-0.001571911**

(e) DISPEX 1.3 % (SERINA FILLER 2)

MASS OF FILLED PYKNOMETER (g)	MASS OF SUPERNATANT (g) (Filled - Empty)	TEMPERATURE MEASURED AT WEIGHING (°C)	CALCULATED VOLUME OF PYKNOMETER (g)	DENSITY OF SUPERNATANT (g/cc) Mass dispersant / Vol. of pyknometer	CALCULATED DENSITY OF WATER AT SAME TEMPERATURE AS DURING WEIGHING THE SUPERNATANT (g/cc)	ERROR IN DENSITY (g/cc) (Dispersant - Water)	PERCENTAGE ERROR IN DENSITY (%)
40.5258	24.2897	21.1	24.3319	0.998265	0.997974	0.000291	0.029157862
40.5257	24.2896	21.1	24.3319	0.998261	0.997974	0.000287	0.028746283
40.5248	24.2887	21.1	24.3319	0.998224	0.997974	0.000250	0.025041922
40.5250	24.2889	21.1	24.3319	0.998232	0.997974	0.000258	0.025865137
40.5252	24.2891	21.2	24.3320	0.998237	0.997952	0.000284	0.028480433
40.5249	24.2888	21.2	24.3320	0.998224	0.997952	0.000272	0.027245647
					Average:	0.000274	0.027422881

(f) DISPEX 1.3 % (AMAZONE COATER)

MASS OF FILLED PYKNOMETER (g)	MASS OF SUPERNATANT (g) (Filled - Empty)	TEMPERATURE MEASURED AT WEIGHING (°C)	CALCULATED VOLUME OF PYKNOMETER (g)	DENSITY OF SUPERNATANT (g/cc) Mass dispersant / Vol. of pyknometer	CALCULATED DENSITY OF WATER AT SAME TEMPERATURE AS DURING WEIGHING THE SUPERNATANT (g/cc)	ERROR IN DENSITY (g/cc) (Dispersant - Water)	PERCENTAGE ERROR IN DENSITY (%)
40.5212	24.2851	22.3	24.3331	0.998029	0.997705	0.000323	0.032405941
40.5199	24.2838	22.6	24.3334	0.997964	0.997636	0.000328	0.032828806
40.5243	24.2882	21.7	24.3325	0.998180	0.997842	0.000338	0.033890924
40.5249	24.2888	21.7	24.3325	0.998205	0.997842	0.000363	0.036360362
40.5192	24.2831	22.7	24.3335	0.997931	0.997613	0.000318	0.031892039
40.5228	24.2867	22.0	24.3328	0.998106	0.997774	0.000332	0.033308665
					Average:	0.000334	0.033447789

(g) FLOCCOTAN 0.3 % (DINKEY FILLER; D_{max} 50 µm)

MASS OF FILLED PYKNOMETER (g)	MASS OF SUPERNATANT (g) (Filled - Empty)	TEMPERATURE MEASURED AT WEIGHING (°C)	CALCULATED VOLUME OF PYKNOMETER (g)	DENSITY OF SUPERNATANT (g/cc) Mass dispersant / Vol. of pyknometer	CALCULATED DENSITY OF WATER AT SAME TEMPERATURE AS DURING WEIGHING THE SUPERNATANT (g/cc)	ERROR IN DENSITY (g/cc) (Dispersant - Water)	PERCENTAGE ERROR IN DENSITY (%)
40.5163	24.2802	22.1	24.3329	0.997835	0.997751	0.000084	0.008431561
40.5140	24.2779	22.3	24.3331	0.997733	0.997705	0.000028	0.00275895
40.5132	24.2771	22.5	24.3333	0.997692	0.997659	0.000033	0.003304432
40.5176	24.2815	21.6	24.3324	0.997908	0.997864	0.000045	0.004463274
40.5166	24.2805	21.8	24.3326	0.997859	0.997819	0.000040	0.004043238
40.5165	24.2804	21.9	24.3327	0.997851	0.997797	0.000055	0.005495846
					Average:	0.000047	0.00474955

Tables 4.2.1.1.2.1 continued: (h) – (i)

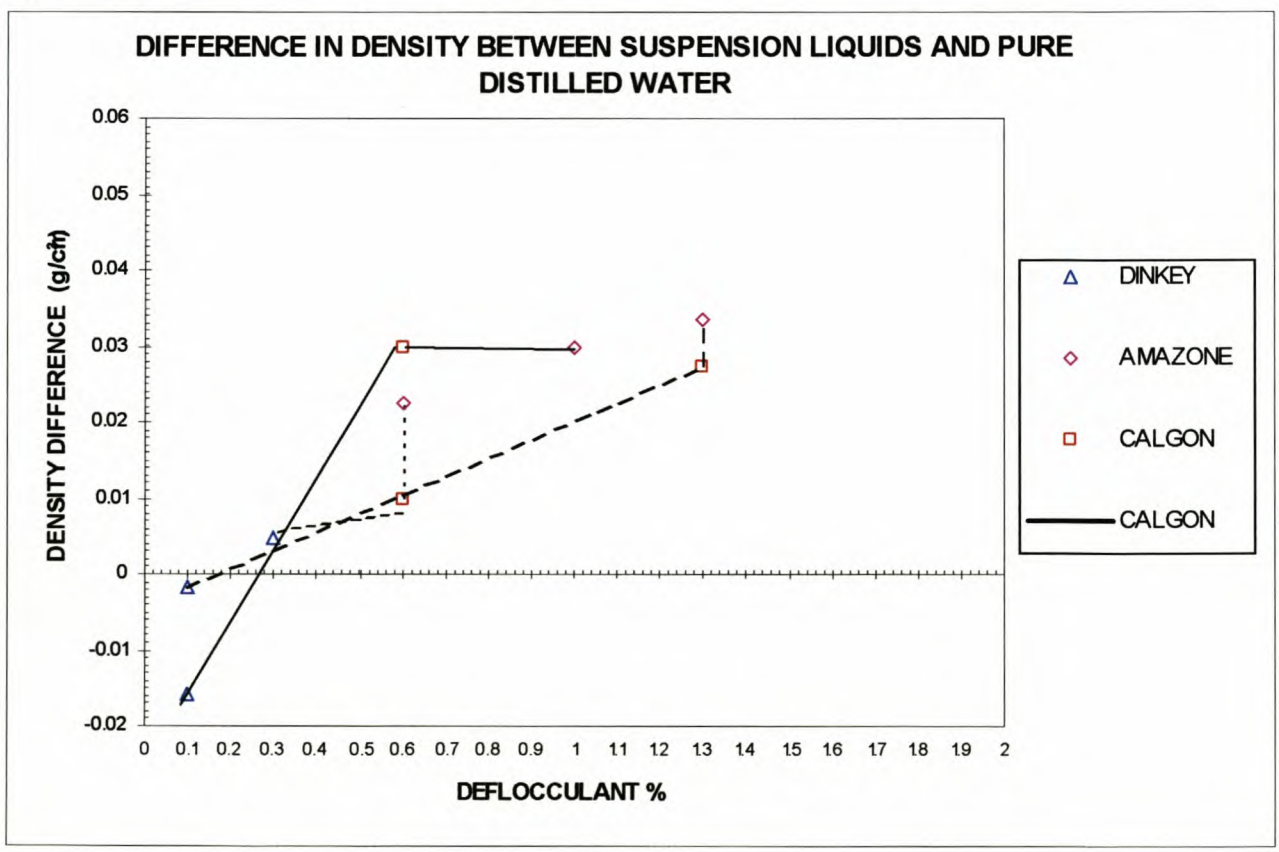
(h) FLOCCOTAN 0.6 % (SERINA FILLER 2)

MASS OF FILLED PYKNOMETER (g)	MASS OF SUPERNATANT (g) (Filled - Empty)	TEMPERATURE MEASURED AT WEIGHING (°C)	CALCULATED VOLUME OF PYKNOMETER (g)	DENSITY OF SUPERNATANT (g/cc) Mass dispersant / Vol. of pyknometer	CALCULATED DENSITY OF WATER AT SAME TEMPERATURE AS DURING WEIGHING THE SUPERNATANT (g/cc)	ERROR IN DENSITY (g/cc) (Dispersant - Water)	PERCENTAGE ERROR IN DENSITY (%)
40.5152	24.2791	22.3	24.3331	0.997782	0.997705	0.000077	0.007701337
40.5149	24.2788	22.4	24.3332	0.997766	0.997682	0.000084	0.00838096
40.5141	24.2780	22.6	24.3334	0.997725	0.997636	0.000089	0.008946707
40.5185	24.2824	21.8	24.3326	0.997938	0.997819	0.000118	0.011867518
40.5179	24.2818	22.0	24.3328	0.997905	0.997774	0.000131	0.013135663
40.5170	24.2809	22.0	24.3328	0.997868	0.997774	0.000094	0.009430422
					Average:	0.000099	0.009910435

(i) FLOCCOTAN 0.6 % (AMAZONE COATER)

MASS OF FILLED PYKNOMETER (g)	MASS OF SUPERNATANT (g) (Filled - Empty)	TEMPERATURE MEASURED AT WEIGHING (°C)	CALCULATED VOLUME OF PYKNOMETER (g)	DENSITY OF SUPERNATANT (g/cc) Mass dispersant / Vol. of pyknometer	CALCULATED DENSITY OF WATER AT SAME TEMPERATURE AS DURING WEIGHING THE SUPERNATANT (g/cc)	ERROR IN DENSITY (g/cc) (Dispersant - Water)	PERCENTAGE ERROR IN DENSITY (%)
40.5268	24.2907	20.6	24.3314	0.998326	0.998082	0.000244	0.024468873
40.5256	24.2895	20.8	24.3316	0.998269	0.998039	0.000230	0.023020541
40.5244	24.2883	20.9	24.3317	0.998216	0.998018	0.000198	0.019842141
40.5245	24.2884	21.1	24.3319	0.998212	0.997974	0.000238	0.023807074
40.5230	24.2869	21.3	24.3321	0.998142	0.997930	0.000212	0.021227192
40.5228	24.2867	21.4	24.3322	0.998130	0.997908	0.000222	0.02221673
					Average:	0.000224	0.022430425

Fig. 4.2.1.1.2.1



This pattern, therefore, is completely the reverse of what was expected. Amazone coater, as the finest kaolinite, has the largest total surface area. Hence, it should adsorb the most anions, and therefore should have removed the largest amount of deflocculant molecules from the suspension liquid. On this account the densities for the Amazone supernatants are expected to be lower than the others – but the opposite is true. To confuse the issue even further two values of the Dinkey coater supernatant (with Dispex and Calgon) had even lower densities than that of water (see Table 4.2.1.1.2.1 (a) and (d) and Fig. 4.2.1.1.2.1).

An obvious explanation for this unexpected pattern is that Amazone coater generally has the highest deflocculant concentrations (Calgon 1.0%, Dispex 1.3%, Floccotan 1.9%), Serina filler 2 has the intermediate concentrations (Calgon 0.6%, Dispex 1.3%, Floccotan 0.6%) and Dinkey coater the lowest (Calgon 0.1%, Dispex 0.1%, Floccotan 0.3%). Hence, more deflocculant remained after adsorption to Amazone, followed by the kaolinites with less amounts of deflocculants. A feasible explanation for Dinkey coater's two negative errors with Dispex and Calgon is that the deflocculant concentrations are so small that even a slight experimental error could have caused these small negative errors.

Lastly, for all the deflocculant/suspension liquid combinations the differences in density with that of pure water were low enough to be disregarded for cell scan rate calculations. The average errors in density of all the kaolinite/deflocculant combinations ranged in *absolute values* between the small values of 0.000016 g/cm^3 for Dispex with Dinkey coater to only 0.000564 g/cm^3 for Calgon with Amazone coater. This represents very small error percentages between the density of the suspension liquid and that of pure water ranging from 0.00157% to 0.057%.

Even the highest error in density of only 0.057% can be regarded as completely insignificant for securing accurate particle size calculations. Such an error in density does not even make a large enough difference to be adjustable on the Sedigraph scan rate knob.

Conclusions:

The density determinations of the supernatant liquids were conducted at a temperature of around 22 °C. However, the operational temperature of the Sedigraph is higher than that: it ranged between 25 °C to 35 °C. Since the errors in density are so small at 22 °C, those at the maximum operational temperature of the Sedigraph (35 °C) should be insignificant also.

Hence, when the normal procedure is followed, by using the density of pure water during any sedimentary method, it should not have the slightest effect on accuracy.

4.2.1.2 Experimental determination of the viscosity of the suspension liquid

The question this time is whether the deflocculant polymer added to the suspension liquid would similarly alter the viscosity to such an extent that it causes inaccurate results when the viscosity of water is used to calculate scan rates.

In this section, the procedure used to determine the viscosities of each of the kaolinite/deflocculant combinations is described, using the same supernatant liquids. Thereafter, the differences between these and the viscosity of distilled water were calculated to obtain the errors in viscosity.

Materials and methods:

The viscosity determinations were performed with an Obolt viscometer. The latter consists of a reservoir, which can accurately be re-filled to the same volume. To calculate the viscosity, the time for all of the liquid to empty under gravity from the reservoir through a fine capillary, is determined with a stopwatch. The viscosity is directly proportional to the time needed to empty the viscometer, as well as to a viscometer constant that is specific to every individual viscometer. With the Obolt viscometer the *kinematic* viscosity (in *c.stokes*) is calculated by the following formula:

$$\eta_l = T \; x \; K_{Visk} \qquad \text{Eq. 4.2.1.2.1}$$

where T is the time in sec., and K_{Visk} is the specific viscometer's constant.

Contrary to the density determinations, that were conducted under a temperature rise, during viscosity determinations a constant temperature had to be used. To ensure its temperature homogeneity, a liquid experiencing a temperature rise needs to be stirred frequently. But unlike the case with the pycnometer determinations, it was not possible to insert the standard mercury thermometer in the viscometer reservoir to stir it, nor to register the temperature. The K-type thermocouples can be inserted into the Obolt reservoir, but it cannot be used to stir the liquid to homogenise it. In fact, there was no other way of stirring, since the tubes leading to the reservoir is too narrow. Consequently, to obtain the viscosities representing the operational range of the Sedigraph, Obolt viscosity determinations were conducted at two different, and accurately controlled temperatures (25 °C and 35 °C). From these, accurate *average* viscosities were calculated at each chosen temperature.

To secure a constant temperature the viscometer was completely immersed in a water bath. During a preliminary trial, using the same standard mercury thermometer as with the

density determinations, the temperature of the water bath was shown to be constant with a less than 0.1 °C variation.

Two series of viscosity measurements were performed with each suspension liquid, at each of the two temperatures. Each series consisted of 5 repeated runs. The viscometer was filled with a supernatant liquid, and immersed until the same temperature as that of the water bath was register right through the viscometer reservoir. The temperature comparison was carried out by means of two type K thermocouples. The preliminary test also showed that when the bath temperature changed, the two type K thermocouples registered temperature changes at exactly the same moment.

At temperature equilibrium, the viscometer reservoir was opened, and the time to empty it recorded with a stopwatch (Tables 4.2.1.2.1 (a) and (b)). Afterwards the average time was calculated for each series. Then the kinematic viscosities were calculated using Eq. 4.2.1.2.1, and noted in the same tables.

From Tables 4.2.1.2.1 (a) and (b) the kinematic viscosities were transferred to new Tables 4.2.1.2.2 (a) and (b), and the errors calculated if the kinematic viscosity of pure water was used instead of that of the suspension liquids. From this the % errors in kinematic viscosity, when the viscosity of water is used, were finally calculated. The kinematic viscosities of pure water at 25 °C and 35 °C, for the latter calculation, were obtained from Table 1.4.2.1.

Results and Discussion:

Tables 4.2.1.2.2 (a) and (b) and Figures 4.2.1.2.1 (a) and (b) disclose that the higher temperature (35 °C), the % errors in kinematic viscosity of all kaolinite/deflocculant combinations enlarge with about 0.5%.

There was furthermore no distinct pattern regarding the errors in kinematic viscosity: Calgon, Dispex, and Floccotan gave more or less similar smallest errors with Dinkey coater ($D_{max\,50}$ μm), Serina filler 2, and Amazone coater. The largest % error in kinematic viscosity of all (1.06%) was registered for Dispex with Serina filler 2 at 35 °C.

It can lastly be seen in Tables 4.2.1.2.2 (a) and (b) that the % errors in kinematic viscosity are much larger than those of the density errors by an order of between 10 and 10^2 (compare with Tables 4.2.1.1.2.1 (c) and (d)). Between 21 °C and 23 °C, the average % error in *density* fluctuated with only 0.0016% to 0.057% in absolute value. However, the % errors in *kinematic viscosity* at 25 °C the varied between −0.29% and 0.51%, whereas at 35 °C it varied between −0.09% and 1.06%.

Conclusions:

1. There is an increase in the error in viscosity with a rise in temperature. This indicates that if the viscosity of pure water is used to calculate the cell scan rate, it can be expected that the largest error in cmp will be encountered when the Sedigraph reaches its highest operational temperature of 35 °C.

The errors in viscosity are much greater than the errors in density. Consequently, the *viscosity* value of pure water will have the largest impact on the error in cmp if the cell scan rate is calculated using the density and viscosity of pure water instead of those of the suspension liquids.

Table 4.2.1.2.1. Determination of Kinematic Viscosity of the supernatent liquids of Serina, Dinkey and Amazone kaolinite suspensions, when dispersed with Calgon, Dispex and Floccotan.

(a) MEASUREMENTS DONE AT 25 °C

TIME (In Sek.) FOR KINEMATIC VISCOSITY MEASUREMENT OF DIFFERENT SUPERNATANT LIQUIDS WITH DIFFERENT KAOLINITES								
DINKEY			SERINA			AMAZONE		
CALGON 0.1%	DISPEX 0.1%	FLOCCOTAN 0.3%	CALGON 0.6%	DISPEX 1.3%	FLOCCOTAN 0.6%	CALGON 1.0%	DISPEX 1.3%	FLOCCOTAN 1.9%
312.93	311.06	311.88	310.55	311.86	310.39	311.21	311.63	312.60
313.18	310.81	311.74	310.64	312.08	310.50	311.37	311.31	312.60
312.68	310.79	311.76	310.39	312.00	310.41	311.19	311.47	312.67
312.64	310.96	311.74	310.72	311.93	310.19	311.28	311.38	312.69
312.75	310.87	311.79	310.61	312.01	310.33	311.66	311.53	312.55
AV. TIME (Sek.) FOR VISCOS. MEASUREM.:			AV. TIME (Sek.) FOR VISCOS. MEASUREM.:			AV. TIME (Sek.) FOR VISCOS. MEASUREM.:		
312.84	310.90	311.78	310.58	311.98	310.36	311.34	311.46	312.62
AV. KINEMATIC VISCOSITY (C.Stokes): (AVERAGE TIME x VISCOSITY CONSTANT (0.002858))			AV. KINEMATIC VISCOSITY (C.Stokes): (AVERAGE TIME x VISCOSITY CONSTANT (0.002858))			AV. KINEMATIC VISCOSITY (C.Stokes): (AVERAGE TIME x VISCOSITY CONSTANT (0.002858))		
0.8941	0.8885	0.8911	0.8876	0.8916	0.8870	0.8898	0.8902	0.8935

(b) MEASUREMENTS DONE AT 35 °C

TIME (In Sek.) FOR KINEMATIC VISCOSITY MEASUREMENT OF DIFFERENT SUPERNATANT LIQUIDS WITH DIFFERENT KAOLINITES								
DINKEY			SERINA			AMAZONE		
CALGON 0.1%	DISPEX 0.1%	FLOCCOTAN 0.3%	CALGON 0.6%	DISPEX 1.3%	FLOCCOTAN 0.6%	CALGON 1.0%	DISPEX 1.3%	FLOCCOTAN 1.9%
254.12	252.14	252.99	252.13	254.81	252.17	253.17	252.91	254.50
253.97	252.20	252.93	252.06	254.94	252.08	253.13	252.81	254.41
254.01	252.18	252.93	251.85	254.84	252.08	253.11	252.85	254.56
253.90	252.09	252.91	251.90	254.95	252.08	252.95	253.02	254.52
254.17	252.14	252.96	252.05	255.00	252.02	253.11	252.96	254.54
AV. TIME (Sek.) FOR VISCOS. MEASUREM.:			AV. TIME (Sek.) FOR VISCOS. MEASUREM.:			AV. TIME (Sek.) FOR VISCOS. MEASUREM.:		
254.03	252.15	252.94	252.00	254.91	252.09	253.09	252.91	254.51
AV. KINEMATIC VISCOSITY (C.Stokes): (AVERAGE TIME x VISCOSITY CONSTANT (0.002858))			AV. KINEMATIC VISCOSITY (C.Stokes): (AVERAGE TIME x VISCOSITY CONSTANT (0.002858))			AV. KINEMATIC VISCOSITY (C.Stokes): (AVERAGE TIME x VISCOSITY CONSTANT (0.002858))		
0.7260	0.7206	0.7229	0.7202	0.7285	0.7205	0.7233	0.7228	0.7274

Table 4.2.1.2.2. Calculation of the error if the kinematic viscosity of water is used in place of that of the supernatant liquids of Serina filler 2, Dinkey coater (D_{max} 50 μm), and Amazone coater (dispersed with Calgon, Dispex and Floccotan).

(a) Experimental temperature: 25 °C

Kin. Visc. of H_2O at 25 °C: 0.889544 (C.Stokes)

SUPERNATANT CONCENTRATION (%)	SUPERNATANT *KINEMATIC* VISCOSITY (C.Stokes)	ERROR IN *KIN.* VISC. (SUPERNATANT - H2O) (C.Stokes)	PERCENTAGE ERROR IN *KIN.* VISC. (%)
CALGON 0.6% (SERINA)	0.887638	-0.001906	-0.21
CALGON 0.1% (DINKEY)	0.894097	**0.004553**	**0.51**
CALGON 1.0% (AMAZONE)	0.889810	0.000266	0.03
DISPEX 1.3% (SERINA)	0.891639	0.002095	0.23
DISPEX 0.1% (DINKEY)	0.888552	-0.000992	-0.11
DISPEX 1.3% (AMAZONE)	0.890153	0.000609	0.07
FLOCCOTAN 0.6% (SERINA)	0.887009	**-0.002535**	**-0.29**
FLOCCOTAN 0.3% (DINKEY)	0.891067	0.001523	0.17
FLOCCOTAN 1.9% (AMAZONE)	0.893468	0.003924	0.44

Fig. 4.2.1.2.1 (a). Error in Kinematic Viscosity at 25 °C

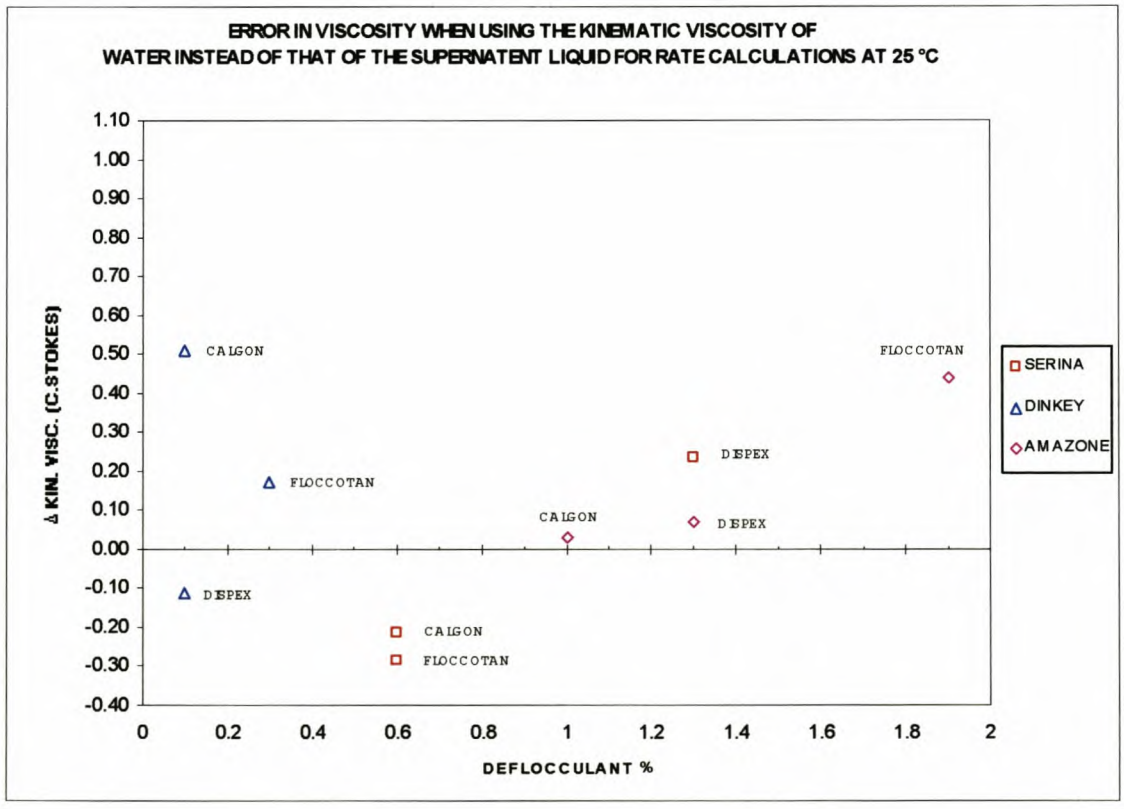
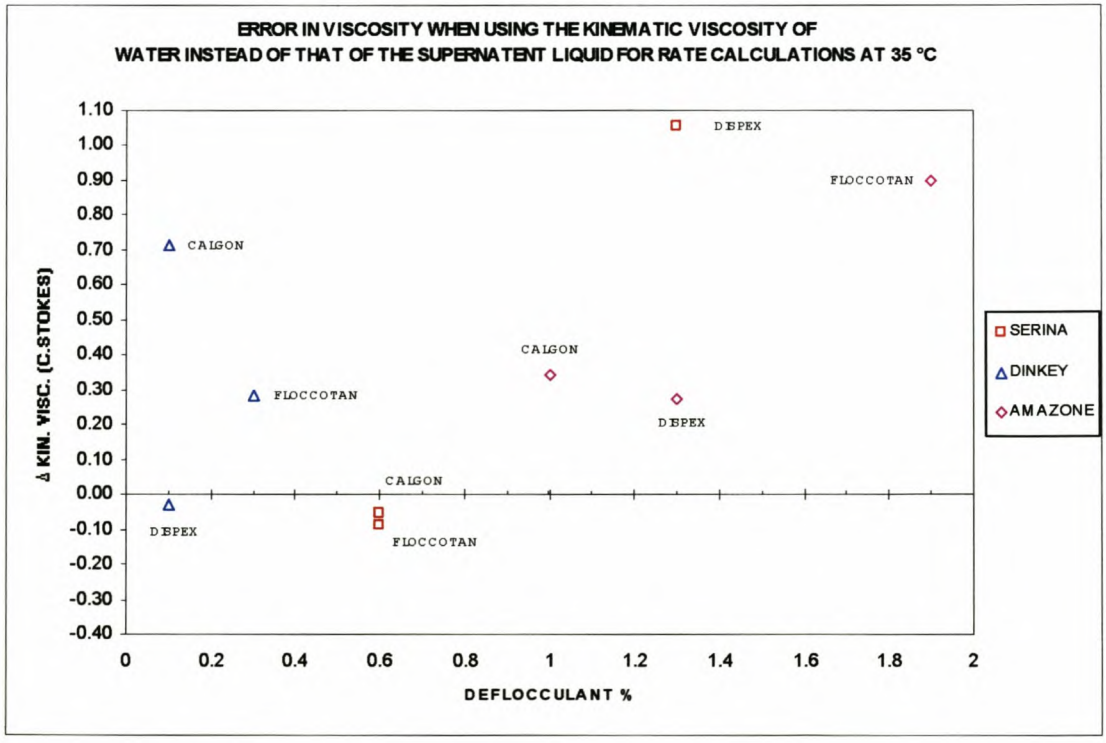


Table 4.2.1.2.2 (b). Experimental temperature: 35 °C

		Kin. Visc. of H_20 at 35 °C: 0.720839 (C.Stokes)	
SUPERNATANT CONCENTRATION (%)	**SUPERNATANT *KINEMATIC* VISCOSITY** (C.Stokes)	**ERROR IN *KIN.* VISC.** (SUPERNATANT - H2O) (C.Stokes)	**PERCENTAGE ERROR IN *KIN.* VISC.** (%)
CALGON 0.6% (SERINA)	0.720216	**-0.000623**	**-0.09**
CALGON 0.1% (DINKEY)	0.726029	0.005190	0.71
CALGON 1.0% (AMAZONE)	0.723331	0.002492	0.34
DISPEX 1.3% (SERINA)	0.728533	**0.007694**	**1.06**
DISPEX 0.1% (DINKEY)	0.720645	-0.000194	-0.03
DISPEX 1.3% (AMAZONE)	0.722817	0.001978	0.27
FLOCCOTAN 0.6% (SERINA)	0.720473	-0.000366	-0.05
FLOCCOTAN 0.3% (DINKEY)	0.722903	0.002064	0.29
FLOCCOTAN 1.9% (AMAZONE)	0.727390	0.006551	0.90

Fig. 4.2.1.2.1 (a). Error in Kinematic Viscosity at 35 °C



4.2.1.3 Calculating the error in cmp when the density and viscosity of distilled water are used to determine scan rates

Both density and viscosity of the suspension liquid of all the kaolinite/ deflocculant combinations have now been experimentally obtained. Hence, the error in *cell scan rate*, if the density and viscosity of distilled water is used to calculate it, can now be secured. Thus the original reason for conducting density and viscosity determinations on the supernatant liquids can be fulfilled *viz.* calculating the *errors in cmp <2 μm* caused by using the density and viscosity values of distilled water in rate calculations.

Methods:

The viscosities calculated previously (Tables 4.2.1.3.2 (a) and (b)), as well as those determined by the Obolt viscometer, are both *kinematic* viscosities (given in c.stokes). However, to calculate the cell scan rate with Eq. 1.4.2.1, the *dynamic* viscosity in c.poise is needed. The dynamic viscosities of the suspension liquids can be calculated with the following equation by using the densities and kinematic viscosities values determined experimentally in sections 4.2.1.1.2 and 4.2.1.3:

$$\text{Dynamic Viscosity (c.poise)} = \text{Kinematic Viscosity (c.stokes)} \times \text{Density (g/cm}^3\text{)} \qquad \text{Eq. 4.2.1.3.1}$$

To be able to use the above equation at the limits of the operational temperature range of the Sedigraph 5000D, the density values of all the *supernatant liquids* at precisely 25 °C and 35 °C were required. These were calculated from the densities of the supernatant liquids already computed in Table 4.2.1.1.2.1 (a) to (i) in the following manner: First, a formula for each relationship between temperature and density were acquired with CurveExpert software. With these formulas, the densities at 25 °C and 35 °C were computed for the supernatant of each deflocculant/ kaolinite combination. These, along with their kinematic viscosities, were used to calculated their dynamic viscosities with Eq. 4.2.1.3.1. The latter values were added to new Tables 4.2.1.3.1 (a) and (b). Using the densities and dynamic viscosities calculated like this, the *correct cell scan rates* at 25 °C and 35 °C were computed for each suspension liquid of each kaolinite/deflocculant combination. Subtracting the cell scan rate *based on pure water*, from these *correct* cell scan rates the errors in cell scan rate were then calculated.

Table 4.2.1.3.1 (a). Error in cmp < 2 μm at 25 °C if the density and viscosity of pure water are used, instead of that of the suspension supernatant liquids for the calculations of Sedigraph rate.

EXPERIMENTAL TEMPERATURE : 25 °C

	Rate H_2O at 25 °C =	Dyn. Visc. of H_2O at 25 °C:
30 μm:	168.46	0.886918
50 μm:	467.95	(C.Poise)

SUPERNATANT CONCENTRATION (%)	CORRECT RATE FOR SUPERNATANT	ERROR IN RATE (RATE DIFFERENCE: SUPERNATANT - H2O)	ERROR IN CMP < 2μ (%)	ERROR IN *DYN.* VISC. (SUPERNATANT - H2O) (C.Poise)	PERCENTAGE ERROR IN *DYN.* VISC. (%)
CALGON 0.6% (SERINA)	168.61	0.15	0.04	-0.001219	-0.14
CALGON 0.1% (DINKEY)	465.01	-2.93	**-1.05**	0.005196	**0.58**
CALGON 1.0% (AMAZONE)	168.27	-0.19	0.00	0.000720	0.08
DISPEX 1.3% (SERINA)	168.20	-0.26	-0.06	0.001635	0.18
DISPEX 0.1% (DINKEY)	468.67	0.72	**0.26**	-0.001224	-0.14
DISPEX 1.3% (AMAZONE)	168.21	-0.25	0.00	0.001047	0.12
FLOCCOTAN 0.6% (SERINA)	169.23	0.77	0.19	-0.003467	**-0.39**
FLOCCOTAN 0.3% (DINKEY)	466.68	-1.27	**-0.45**	0.002071	0.23
FLOCCOTAN 1.9% (AMAZONE	167.49	-0.97	-0.02	0.004683	0.53

Fig. 4.2.1.3.1 (a). Error in cmp < 2 μm at 25 °C

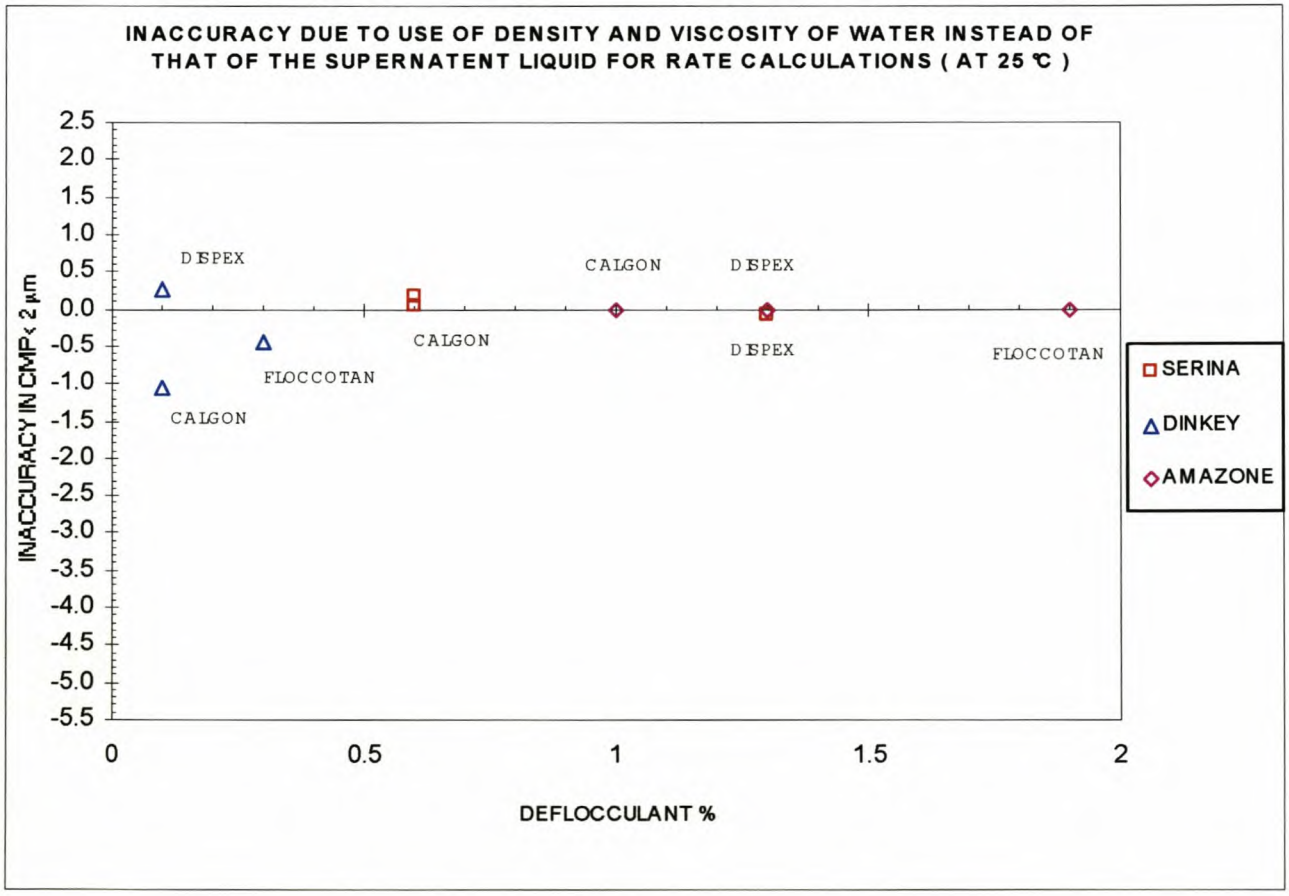


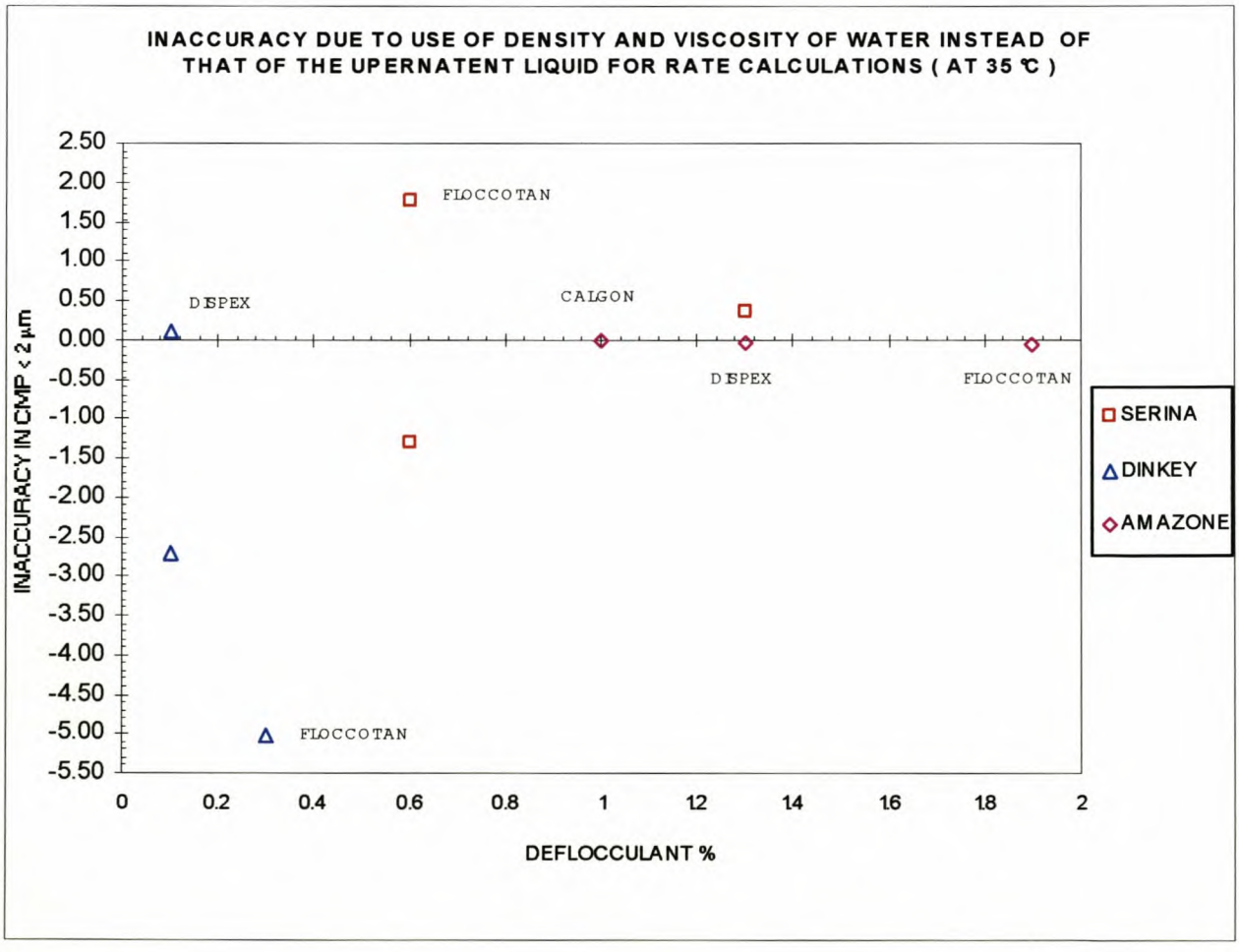
Table 4.2.1.3.1 (b). Error in cmp < 2 μm at 35 °C if the density and viscosity of pure water are used, instead of that of the supernatant liquids for the calculations of Sedigraph rate

TABLE 5.2.1.3.1 (b) EXPERIMENTAL TEMPERATURE: 35 °C

	Rate H_2O at 35 °C =	Dyn. Visc. of H_2O at 35 °C:
30 μm:	208.90	0.716539
50 μm:	580.28	(C.Poise)

SUPERNATANT CONCENTRATION (%)	CORRECT RATE FOR SUPERNATANT	ERROR IN RATE (RATE DIFFERENCE: SUPERNATANT - H2O)	ERROR IN CMP < 2μ (%)	ERROR IN *DYN.* VISC. (SUPERNATANT - H2O) (C.Poise)	PERCENTAGE ERROR IN *DYN.* VISC. (%)
CALGON 0.6% (SERINA)	203.43	-5.47	**-1.32**	0.011629	1.60
CALGON 0.1% (DINKEY)	572.68	-7.61	**-2.72**	0.007865	1.09
CALGON 1.0% (AMAZONE)	208.19	-0.71	-0.01	0.002460	0.34
DISPEX 1.3% (SERINA)	210.39	1.48	0.36	-0.000307	-0.04
DISPEX 0.1% (DINKEY)	580.60	0.32	0.11	-0.000315	-0.04
DISPEX 1.3% (AMAZONE)	207.30	-1.60	-0.03	0.004174	0.58
FLOCCOTAN 0.6% (SERINA)	216.26	7.36	**1.77**	-0.015494	**-2.21**
FLOCCOTAN 0.3% (DINKEY)	566.26	-14.03	**-5.01**	0.011738	**1.61**
FLOCCOTAN 1.9% (AMAZONE	205.73	-3.17	-0.06	0.009319	1.28

Fig. 4.2.1.3.1 (b). Error in cmp < 2 μm at 35 °C



Ultimately, the regression formulas of error in cmp against errors in cell scan rate of Tables 3.2.2.1.1.1 (b) to 3.2.2.1.1.4 (b), and Table 3.2.2.1.1.5 (tests on the apparatus parameters) were transferred to Tables 4.2.1.3.1 (a) and (b). By using these regression formulas, the errors in cell scan rate were translated into the *errors in cmp*. These errors, caused when the density and viscosity of pure water are used in cell scan rate calculations, are given in Figures 4.2.1.3.1 (a) and (b).

Results and Discussion:

The densities of the suspension liquids calculated by the regression formulas could not be as accurate as one could have hoped for. The reason is that their pycnometric determinations were conducted over temperatures ranging between 21°C and 23 °C. This temperature range is too small to give a regression formula that can be used accurately to calculate accurate densities at the much higher temperature of 35 °C. To obtain an accurate regression formula usable at 35 °C, the temperature rise during pycnometric density determinations should preferably have been between 25 °C and 35 °C. These would have allowed the calculation of more accurate dynamic viscosities. This in turn would have given more accurate errors in cmp than currently is the case (Table 4.2.1.3.1 (b)).

The question is now: is the *errors in cmp* at 35 °C accurate enough to evaluate the validity of the use of the distilled water properties to calculate scan rates at that temperature? To answer this question, the accuracy of the calculated *errors in cmp* can be evaluated in an indirect manner. This is accomplished by comparing the accuracy of the suspect *dynamic* viscosities in Tables 4.2.1.3.1 (a) and (b) (calculated from the *kinematic* viscosities by using the suspect density values) with that of the more precise, experimentally obtained *kinematic* viscosities in Tables 4.2.1.2.2 (a) and (b) of the previous section. In this way, the *errors in cmp*, ultimately calculated from these suspect *dynamic* viscosities, are simultaneously put to the test.

At 25 °C, the maximum % errors in kinematic and dynamic viscosities were 0.51% and 0.58%, respectively. At 35 °C, the maximum % errors in kinematic and dynamic viscosities were 1.06% and 1.61% respectively. This size of the discrepancy at 35 °C implies that the calculated errors in cmp can be accepted for the time being. It can therefore be used to indicate how much accuracy will be affected should the density and viscosity of pure water be used to calculate cell scan rates.

The last step is to test the validity of using the density and viscosity of distilled water to calculate cell scan rate. To accomplish this the largest cmp errors caused by it need to be inspected:

At 25 °C the maximum errors in cmp < 2 μm was the −0.45% for Dinkey coater ($D_{max\,50}$ μm) with Floccotan, and −1.05% for Dinkey coater (D_{max} 50 μm) with Calgon. For the rest of the kaolinite/ deflocculant combinations the cmp errors were still acceptable.

At 35 °C the largest cmp error of all was the 5.78% for Dinkey coater ($D_{max\,50}$ μm) when dispersed with Floccotan. At 35 °C, three other combinations similarly gave unacceptable results: Serina filler with Calgon (an 1.50% cmp error), Serina filler with Floccotan (an 1.57% cmp error), and Dinkey coater with Calgon (an cmp 3.50% error). From these error values one can also deduct that as temperature increases the error in cmp grew.

Finally, an attempt was made to offer a reason for the pattern of the cmp errors for the different kaolinite/deflocculant combinations. At 25 °C, the kaolinite type that has the largest cmp errors is Dinkey Coater (D_{max} 50 μm). It has a −1.05% cmp error when deflocculated with Calgon, a cmp error of −0.45% with Floccotan, and an error of 0.26% when deflocculated with Dispex. The pattern at 35 °C appears to support this observation. It is therefore clear that at least one kaolinite type – Dinkey Coater (D_{max} 50 μm) – will exhibit observable errors in cmp < 2 μm should the densities and viscosities of water be used in place of its real suspension liquid values.

However, this kaolinite had the *lowest deflocculant concentration* of all the kaolinite types investigated here. Hence, logically, the densities and viscosities of Dinkey Coater (D_{max} 50 μm) supernatants should be closest to that of distilled water. It should therefore have given rise to the smallest errors in cmp. Yet, it gave the largest errors or all the kaolinite types tested here. It therefore appears that the error in cmp is more a function of the kaolinite type than it is of its deflocculant concentration.

In stark contrast, though, Amazone coater gave the *smallest* error in cmp despite the fact that it had the *highest deflocculant concentrations* of all. A reasonable explanation for this is that Amazone, being much finer than the other two, needed more deflocculant to disperse. This is since with its higher total particle surface it adsorbed more deflocculant from solution. Hence, the densities and viscosities of Amazone suspension liquids are closer to that of water. For that reason, Amazone has smaller errors in cmp when the density and viscosity of water are used for its scan rate calculations. However, Dinkey coater, being nearly as fine as

Amazone, should then have given better results than the coarsest kaolinite *viz.* Serina filler. No reason for the above pattern in the cmp errors can be offered.

Conclusions:

1. When the density and *viscosity* of pure water were used for cell scan rate calculations instead of that of its suspension liquids at the operational temperature range of the Sedigraph, then Dinkey coater (D_{max} 50 μm) gave large enough errors in cmp to noticeably influence its accuracy.
2. The *density* values of all the suspension liquids were close to that of water. Therefore, to completely safeguard accuracy, it can safely be said that *only the viscosity values* of the supernatants need to be determined experimentally. But the procedures of ultracentrifugation, density, and viscosity determinations, are very time consuming. This should therefore only be done if the expected cmp errors of between −5.01% and 1.77% cannot be tolerated. To save time the viscometer can be calibrated to supply dynamic viscosity directly. A little bit less accurate will be to use the density and viscosity of the clean deflocculant at 1.5%. This can beforehand be determined over the temperature range of the Sedigraph, and used in place of that of water.
3. Swell-clay, and especially illite, have larger anion exchange capacities than kaolinite (van Olphen, 1977). It can therefore be expected that swell-clays will potentially remove much more deflocculant molecules from suspension than kaolinite. Therefore for most soils, the inaccuracy should be noticeably less when the density and viscosity of the suspension liquid are not used for scan rate calculations.
4. When deflocculant polymers are dissolved in water, its viscosity rises slightly faster with the rise in temperature than is the case with the viscosity of pure water. Consequently, should the viscosity of pure water be used for cell scan rate calculations, then higher errors in cmp is encountered later in the day at the final operational temperature of 35 °C (see conclusion 1 in the previous section).
5. During all analyses of this study to discover the effect on accuracy and reproducibility of the *other parameters*, absolute accuracy was of no importance. Comparability was the only vital issue. On this account, the density and viscosity of *distilled water* was be used to calculate their cell scan rates. In this way, much time was saved, since the elaborate procedures to get hold of the true densities and viscosities were avoided.

Recommendations for further study:

1. The errors in cmp calculated above can be regarded as fairly accurate. But it is advisable to recalculate the dynamic viscosity by using more accurate experimental density values.

   At 25 °C Dinkey with Calgon and Floccotan gave the highest errors in viscosity, and the largest errors in cmp. According to this, only the pycnometric density values of Dinkey with Calgon and Floccotan combinations need to be re-determined over the temperature range 25 °C to 35 °C. This can afterwards be used to secure regression formulas for their density against temperature, which are accurate past 35 °C.

   Then, with density values that are more accurate now available at both 25 °C and 35 °C, dynamic viscosities can be calculated that is more accurate. This will supply more accurate values for the largest cmp errors that can be expected when using the density and viscosity of water. With this in hand, a more accurate assessment can be made whether the density as well as the viscosity of pure water can be used in place of that of the suspension liquid.

2. If the latter test is positive, then an additional test must be carried out to find out whether the viscosities of the optimum deflocculant solutions *as-is* (without first adding the clay) can be used for viscosity determinations, in place of their supernatant solutions. This will save the time consuming procedures necessary to first conduct density and viscosity determinations on every suspension liquid with every analysis that needs to be very accurate.

   Further time can be saved by constructing viscosity curves at a few temperatures in the widest possible operational range of the Sedigraph (17 °C to 56 °C). This will cover any room temperature, which is expected to range between 10 °C and 40 °C (the Sedigraph operational temperature reaches between 7 °C to 16 °C higher than room temperature). First, the viscosities of each optimum deflocculant concentration can be determined at a few temperatures covering this temperature range. Then, viscosity curves can be acquired by means of regression analysis of the viscosity vs. temperature data.

4.2.1.4 Inaccuracy when water is used to adjust the 0% setting

The 0% setting needs to be adjusted before each analysis. This is carried out to adjust the apparatus to the X-ray intensity with 0% clay in the sample cell: hence the X-ray intensity of the suspension liquid only. Since air has a much lower X-ray absorbency than the suspension liquid, the 0% setting is normally conducted with distilled water in the cell to represent the

clean suspension liquid.

This procedure, however, assumes that the X-ray absorbency of water is close enough to that of the suspension liquid. However, should there be a substantial difference between them, then the 0% adjustment might be inaccurate enough to noticeably affect the particle size analysis results directly following it. For this reason, an experiment was conducted to determine the cmp when the 0% adjustment was made with distilled water. These values were then compared to those when the supernatant liquids of Serina filler 2 were used to adjust the 0% setting. To additionally test the contribution of deflocculant type to X-ray absorbance, the kaolinite was dispersed with three of the deflocculants types *viz.* Calgon, Dispex, and Floccotan.

If the presence of the deflocculant did make a difference, the next question was whether one could use clean deflocculant solution to adjust the 0% setting. This would save the time required for first extract the supernatant by means of centrifugation. However, clean deflocculant solution will have a higher deflocculant concentration than the actual suspension liquid, since in the latter some deflocculant molecules will be adsorbed by its suspended clay particles. Accordingly, this test therefore also included a second set of the same deflocculant solutions at their proper concentrations – but without clay being added.

Materials and Methods:

The X-ray tube was first warmed up to assure a stable X-ray intensity. With the sample cell filled with water, the pen was adjusted until the average of its trace was on the nearest cmp line.

Thereafter the cell was filled with a supernatant liquid of Amazone dispersed with 1.5% Calgon. The pen was allowed enough time to draw its line, and then the average of the pen's trace was noted in Table 4.2.1.4.1. A second run of each was also performed, to ascertain whether the X-ray tube was stable, and the magnitude of the electronic noise constant. This procedure was duplicated for Amazone with Dispex 1.8% and Floccotan 2.3% supernatant liquids, followed by the full strength deflocculant solutions *as-is* (without adding any clay).

The supernatants of Amazone were used since it removes the largest amount of deflocculant due to adsorption (section 4.2.1.3). It was reasoned that they should therefore also influence the X-ray absorbance the most.

Table 4.2.1.4.1. Inaccuracy in cmp due to the use of either distilled water or clean deflocculant sollution in stead of the supernatent liquid of kaolinite suspensions during the 0% setting of the Sedigraph.

INACCURACY IN 0% ADJUSTMENT (CMP OF DISTILLED WATER - CMP OF DEFLOCCULANT)					
DEFLOCCULANT AFTER CLAY WAS REMOVED			DEFLOCCULANT BEFORE CLAY WAS ADDED		
Calgon 1.5%	Dispex 1.8%	Floccotan 2.3%	Calgon 1.5%	Dispex 1.8%	Floccotan 2.3%
1.5 1.5	0 0	0.5 0.5	2 2	0 0	0.5 0.5
Averages:					
1.5	**0**	**0.5**	**2**	**0**	**0.5**

Results and Discussion:

The results first of all disclose that only with Calgon the use of water to adjust the 0% setting should bring about noticeably inaccurate results. The 0% setting when adjusted with water differed with 1.5% cmp from that when the supernatant of the Calgon suspension was used. Furthermore, when water was used instead of full-strength Calgon, the difference rose slightly to 2% cmp. Therefore, the supernatant and full strength deflocculant solution differed in their affect by only 0.5%. This discrepancy, however, was not enough to warrant the time consuming centrifugation to obtain the supernatant liquids for use with 0% adjustments. The full strength deflocculant solutions can very quickly be made up to adjust the 0% settings instead.

A second run of each revealed that no more repeated runs were needed for any of the deflocculant solutions in order to secure a more accurate average.

Conclusions:

A clean, full-strength Calgon solution, at the same concentration as the clay suspensions, should rather be used instead of water when adjusting the 0% setting. With Dispex and Floccotan distilled water can be used without fear of an error.

Recommendation for further study:

1. Rerun this experiment. But, additionally run three particle size analyses of each sample suspension with the same deflocculant, at the same concentration. With each repeated analysis, adjust the 0% setting with water, supernatant, and full strength deflocculant solution. From these results, calculate the actual errors in cmp when adjusting the 0% with water, as opposed to adjusting it with the supernatants or the full strength deflocculant solutions.
2. Swell-clays have much larger anion exchange capacities than the kaolinite used in the above tests. Hence, it potentially should adsorb much more deflocculant molecules from suspension, than is the case with kaolinite. This should potentially cause smaller errors when the density and viscosity of distilled water is used to calculate particle size, and to adjust the 0% setting. Therefore, it is suggested that the tests of above two sections be repeated for a number of soils with different swell-clay compositions.

   Determine the average cmp error for all of these suspensions. The viscosities and densities of the supernatant liquid giving error values closest to the average errors can then be determined over the operational range of the Sedigraph. These viscosity and density values can thenceforth be used to calculate scan rate of all the following analyses, and the liquid itself can be used to adjust 0% settings of all subsequent analyses.

4.2.2 The influence of the solid concentration on accuracy and reproducibility

Since the Sedigraph uses X-rays, the solid concentration of suspensions needs to be *high* enough to give accurate results. However, with all sedimentation methods the best accuracy is achieved under the free-fall conditions of a *very low* solid concentration (section 1.5.2). It therefore follows that the requirements to satisfy Sedigraph instrument limitations, and the prerequisites of the sedimentary method it uses are in antagonism to each other. Only when the density of the material to be analysed is high enough, this impasse is avoided. The question now arose whether the densities of clays are high enough to satisfy the demand of the Sedigraph 5000D, and simultaneously allow a low enough solid concentration to achieve free-fall conditions.

On this account it was necessary to experimentally determine the magnitude of the effect of hindered settling at the minimum clay solid concentration allowed for the Sedigraph 5000D. The first step was to determine the required solid concentration for the particular instrument

employed during this study. Then, at this solid concentration, the effect on repeatability of hindered settling was demonstrated experimentally.

4.2.2.1 Establishing the correct solid concentration for the Sedigraph 5000D

At the solids content of between 3-4% by volume needed by the Sedigraph 5000D, its particle size distributions should already start to become inaccurate. This is due to the combined effects of particle collisions and hindered settling (section 1.5.2.1.2). Hence, for the Sedigraph the smaller particle sizes will theoretically be registered at lower cmps than Stokes' Law would have predicted, and the middle and larger particle sizes at too large cmp values.

The negative effect of particle interactions on accuracy can be minimised by diluting the suspension. On this account, an attempt was made to reduce the solids content of the Sedigraph as low as possible, while still staying within the accuracy limits of the instrument. The Sedigraph only provides optimum accuracy over a restricted range of transmitted X-ray intensities. The X-ray intensity must be maintained within proper limits. To accomplish this, the suspension concentration must be such that it lowers the transmitted X-ray intensity to between 40-60% of that when the cell is filled with distilled water only. To furthermore ensure a statistically reliable X-ray output, the X-ray intensity meter must never fall below 25 micro amperes at the start of the analysis. Along with this, during 100% adjustments its dial must never be set below 500.

To achieve all of the above criteria, the appropriate solid concentration of every new material needs to be determined beforehand. This is therefore the first step in the particle size analysis of any unknown substance.

Materials and Methods:

In order to determine the optimum solid concentration for kaolinites, a suspension of 10% by weight of Serina filler was made up in a 1.2% Dispex concentration. Firstly, equations 4.1.2.1.1 and 4.1.2.1.2 were used to calculate the volumes of deflocculant stock solution and distilled water to attain a higher solid concentration than expected to be necessary. For this a 9 g Serina filler sample was mixed with 81 cm^3 Dispex solution (18 cm^3 6 g/l stock solution + 63 cm^3 distilled water), to acquire a suspension concentration of 10% by weight (4.05% by volume).

First, the sample cell was filled with distilled water. The X-ray intensity was recorded, with the X-ray intensity adjusted at its maximum value. Thereafter the suspension was

continuously pumped through the cell, and the 100% adjustment made. Both the 100% setting and the X-ray intensity was noted in Table 4.2.2.1.1. The % lowering of the X-ray intensity by the suspension was calculated, by subtracting the intensity of the kaolinite suspension from that of the cell filled with distilled water only. Next, the X-ray intensity was adjusted to minimum intensity, the same values were noted, and the same calculations repeated.

From then on, the sample suspension was stepwise diluted by repeatedly adding 5 ml of distilled water (see Table 4.2.2.1.1). With each step, all the above variables were noted, and the same calculations repeated.

Table 4.2.2.1.1. Determination of the correct solid concentration for Sedigraph 5000D particle size analysis of a kaolinite suspension.

X-RAY INTENSITY	DISTILLED H_2O ADDED (ml)		SOLIDS CONCENTRATION		DISTILLED H_2O IN CELL	CLAY SUSPENSION IN CELL		% LOWERING OF X-RAY I BY THE SUSPENSION
	Amount added	Total	($^{W}/_{W}$) %	($^{V}/_{V}$) %	X-Ray I	100%-Setting	X-Ray I	
min.	0	0	10.00	4.05	38.3	456	21.7	43.34
max.					49.0	470	28.3	42.24
min.	5	5	9.52	**3.85**	38.3	477	22.2	42.04
max.					49.1	**502**	**29.2**	**40.53**
min.	5	10	9.09	3.66	38.4	492	22.8	40.63
max.					49.1	512	29.7	39.51
min.	10	20	8.33	3.34	38.4	548	24.0	37.50
max.					49.0	577	31.3	36.12
min.	20	40	7.14	**2.84**	38.3	650	**25.8**	**32.64**
max.					49.0	691	34.7	29.18
min.	20	60	6.25	2.47	38.3	762	27.3	28.72
max.					49.1	808	35.5	27.70
min.	20	80	5.56	2.19	38.3	870	28.6	25.33
max.					49.1	918	36.9	24.85
min.	10	90	5.26	2.07	38.3	921	29.0	24.28
max.					49.1	965	37.5	23.63
min.	5	95	5.13	**2.01**	38.3	**944**	29.3	**23.50**
max.					49.1	994	37.8	23.01
min.	10	105	4.88	1.91	38.3	997	29.7	22.45
max.					49.1	**>999***	38.4	21.79
min.	5	110	4.76	1.87	38.3	**>999***	29.7	22.45
max.					49.1	**>999***	38.6	21.38
min.	34	144	4.10	**1.60**	38.3	**>999***	31.0	19.06
max.					49.1	**>999***	40.0	18.53

* When trying to adjust to 100%, as the suspension is being pumped through the cell, and the suspension is too diluted. Therefore the 100%-knob is set at maximum (999), while on the graph paper the pen is still below 100%. Hence, any analysis in these cases is meaningless.

Results and Discussion:

The X-ray tube of the instrument used had already lost some intensity due to its age. However, a lower X-ray intensity is an advantage when analysing a material with a relatively low density such as kaolinite. The lower the X-ray intensity the less the solids content of the sample needed to achieve the above criteria for accurate Sedigraph analysis. This in turn

reduces hindered settling, leading to more accurate analyses results (sections 1.5.2.1.2 and 4.2.2.3).

Despite the weak X-ray tube, both the maximum allowable lowering of X-ray intensity by the sample suspension of about 40%, and the minimum allowable 100% setting of 500, were reached at a still relatively high solids content of 3.85% ($^{v}/_{v}$) (9.52 ($^{w}/_{w}$)). The X-ray intensity needed to be adjusted at its highest value to ensure a transmitted intensity above 25 microamperes (Table 4.2.2.1.1).

With three more dilutions, a volume concentration close to 3% was reached. This concentration is regarded as having only marginal errors produced by hindered settling (Instructions Manual Sedigraph 5000D, 1979). Here, however, the minimum allowable X-ray intensity of 25 µA was reached, with an accompanying percentage lowering of the X-ray intensity at only 32.64%, which is beneath the lower limit for accurate analysis of 40%.

Hence a volume concentration of 1% – where free fall conditions are said to still prevail – could therefore also not be reached with the Sedigraph 5000D. Already at a 1.87% volume concentration the highest setting on the 100% dial was reached (999). This was despite the fact that the X-ray intensity was adjusted to its minimum.

Conclusions:

1. A solids content of 3.85% $^{V}/_{V}$ (9.52% $^{W}/_{W}$) gave the lowest kaolinite suspension concentration that can be achieved with the particular instrument used during this study, despite its already weakened X-ray tube.
2. The previous point proves that the density of kaolinite is just too low to reach an acceptable volume concentration of 3%. The latter concentration would only marginally have reduced the accuracy due to high-concentration hindered settling. However, the densities of all soil minerals are close to, or lower than that of kaolinite. Hence the accuracy of all soil particle size analyses will only marginally be curbed by the slightly too high solid concentration called for by the Sedigraph 5000D.
3. The weakening typical of all Sedigraph 5000D X-ray tubes is in good stead for kaolinite size analysis. It will allow increasingly lower suspension concentrations to still stay within the above-mentioned instrument limits for transmitted X-ray intensity and 100% adjustment.

Recommendation for further study:

Determine the surface charge per unit area for each of the kaolinite types, and determine the conductivity of each at the given Dispex concentrations. Then, use this data to decide whether electro-viscosity could have added to the observed ordering in the results between the different kaolinite types.

4.2.2.2 Magnitude of the effect of hindered settling on *accuracy* at the lowest possible clay concentration for the instrument used

Further on in Chapter 5, the influence of Na-montmorillonite on the accuracy of sedimentary particle size analysis is investigated. To prevent montmorillonite from gelation during these tests, a solid concentration of 1.13% by volume, or lower, needs to be employed (Watts *et al.*, 2000). However, the minimum kaolinite solid concentration for the instrument used, was determined at 3.85% by volume (section 4.2.2.1). During the latter test, before the limit of the 100% adjustment was reached at a dial-setting of 999, the solids content could be decreased only to as low as 1.91% by volume, (Table 4.2.2.1.1). This, though, is not a low enough solid concentration to stop Na-montmorillonite from gelling.

There is, however, a way to solve this solid concentration problem on the Sedigraph 5000D. To allow the analysis of particles with a very low X-ray absorbency, the instrument has a switch in the cell compartment that reduces its X-ray intensity 7-fold. By using this switch, the X-ray intensity could be decreased sufficiently, to permit a particle size analyses at much lower solid concentrations than the previously determined minimum of 1.91% by volume (Weaver and Grobler, 1981). At such low solid concentrations, the accuracy of the Sedigraph 5000D should, at least in theory, be sacrificed.

Nevertheless, when Watts *et al.* (2000) compared kaolinite particle size distributions of the later model Sedigraph 5100 with that of the Andreasen pipette method, they used solid concentrations of as low as 0.38%, 0.75%, 1.13%, and 1.50% by volume with both these methods. They found that there was no difference in the results of the two methods at the lowest solid concentration of 0.38%. They therefore concluded that the newer model provides very accurate results – even at clay concentrations lower than that prescribed by the manufacturer. This gave them the ability to analyse Na-montmorillonite at solid concentrations below that which caused it to gel (0.38%, 0.75%, 1.13% and by volume). Welch *et al.* (1979), using the older model Sedigraph 5000D at only 0.42% by volume, similarly obtained excellent comparison with the Andreasen method (section 1.5.2.1.3)

It was therefore decided to switch the X-ray tube of the instrument to its low intensity setting, and then to repeat the test of section 4.2.2.1 to determine the lowest solid concentration of a kaolinite sample. Such a particle size analysis would thus be done at the absolute minimum attainable solid concentration. The possible difference in cmp between this solid concentration and that at the acceptable solid concentration of 3.85% by volume, could then be calculated by comparing it to the results of section 4.2.2.1.

A second reason to conduct this experiment, was to test the magnitude of the effect of hindered settling on accuracy when working at the solid concentration of 3.85% by volume required for the Sedigraph 5000D. At this high concentration, the effect of particle-particle interactions should be enhanced during all analyses.

Materials and Methods:

For this experiment a Serina filler 1 kaolinite sample was made up at the lowest acceptable solid concentration of 3.85% by volume. The same sample was analysed repeatedly at decreasing solid concentrations, until the limit of the 100% setting was reached, which was at 1.91% solids by volume. The particle size distribution for each analysis was recorded at the low-intensity position (Table 4.2.2.2.1).

The results were used to simultaneously demonstrate the reduction in hindered settling which accompanied the reduction of solid concentration to 1.91% by volume (Table 4.2.2.2.1). This was accomplished by comparing the results with that while the X-ray tube was still at the high-intensity position. The latter data was carried over from Table 4.2.2.1.1.

Next, with the X-ray intensity at the low setting, the sample was re-run at the same solid concentration as the last analysis (1.19% by volume). However, during the preliminary 0% and 100% adjustments, it was noted that the electronic noise expanded dramatically. The pen's up-and-down movement at a 100% setting of 750 increased from approximately ± 0.8 % during the high X-ray intensity setting, to a fluctuation of about ± 2.25 % after switching to the lower intensity.

Subsequently, when the analysis itself was done, it was noted that the pen's up-and-down movement was even more amplified, and not harmonious anymore. Consequently, when using the plastic strip to read off the results from the graph, it was very difficult to decide where the average of the pen's fluctuations was situated. This resulted in very inaccurate results (compare the particle size distribution for 1.91% solids by volume between the high and low X-ray intensity switch-settings in Table 4.2.2.2.1).

Table 4.2.2.2.1. Determining the lowest permissable solid concentration for a kaolinite suspension with the Sedigraph 5000D

Deflocculated with 1.5% Dispex

PARTICLE SIZE (μm)	CUMULATIVE MASS PERCENTAGE							
	High I switch-setting							Low I Setting
	3.85% by volume	3.20% by volume	2.74% by volume	2.39% by volume	2.13% by volume	1.91% by volume	Error	(1.91% by volume
2.0	55.4	55.6	55.9	56	55	52	3.4	61
3.0	65.1	65.4	65.9	65.1	64.3	64	1.1	71
4.0	72.3	73.1	72.3	72.3	71.2	71	1.3	76.6
5.0	77.4	78.4	78	77.5	76.6	76	1.4	82.2
6.0	81.9	82.5	82.2	82.3	81.2	81	0.9	85
8.0	88.2	98.5	89	88.4	88	87.7	0.5	87.3
10.0	92.4	93.3	94.5	92.6	92.4	92	0.4	92
20.0	100	99.5	99.8	99.3	99.5	100	0	99.9
30.0	100	100	100	100	10	100	0	100

Thereafter, the suspension was diluted further to the highest concentration used by Watts *et al.* (2000) (0.75% by weight). The electronic noise, however, during the 0% adjustment reached an even larger fluctuation of more or less ± 6% cmp. The distributor of Micromeritics in South Africa ascribed this growth in electronic noise to an electronic problem. Therefore the attempt to dilute the sample to the levels of Watts *et al.,* by utilising the low X-ray intensity switch-setting, had to be call off.

Results and Discussion:

It is clear that with the lowering of clay concentration the particle size distribution stayed more or less constant until 2.39% by weight was reached. But, from 2.13% by volume and lower, the smaller particles (5 μm down to 2 μm) start to exhibit a rapid reduction in cmp. This is to be expected, since when decreasing the solid concentration, the up-flow due to high concentrations hindered settling will less and less retard the settling of the smaller particles. Therefore, as the solid concentration is reduced, the clay concentration – and therefore the cmp values – will accordingly be reduced at the smaller particle sizes.

At 2 μm, the difference between the size of the effect of hindered settling at the minimum

solids permissible by the Sedigraph instructions manual (3.85%), and that at the minimum solids permitted by the 100% setting (1.91%), was 3.4% cmp. The lower solid concentration was therefore noticeably less affected by hindered settling than at the higher concentration value.

Conclusions:

1. The fact that both models of the Sedigraph give the same results as the Andreasen method at very low solid concentration indicates that the low concentration Sedigraph results should be more accurate than those conducted at 3.85% by volume. The reduction in hindered settling obviously had a larger positive effect than the negative effect of moving outside the instrument variables stipulated by the handbook. The errors calculated in Table 4.2.2.2.1 should therefore rather be regarded as an indication of the magnitude of the effect of hindered settling at the solid concentration required by the Sedigraph handbook.
2. Due to the presence of the deflocculant ions, electro-viscosity could additionally have contributed to the higher cmp values at 3.85% ($^{v}/_{v}$) solids. It can be seen from Eq. 1.6.2.1 that the higher the total mass of particles in suspension, the smaller will be the settling velocity due to electro-viscosity. As a result, when electro-viscosity is active, enlarging the particle concentration will add to the effect of hindered settling to induce higher cmp values at all particle sizes.

4.2.2.3 Impact of hindered settling on *repeatability* with the Sedigraph 5000D

Although hindered settling will affect absolute accuracy, particle-particle interactions can theoretically not reduce reproducibility and repeatability to any serious degree. This was already shown to some degree by the low stdev of many repeated analyses of different samples of the same kaolinite type (reproducibility), as well as by the low stdev during repeated analysis of the same sample (repeatability) (*e.g.* Table 4.2.3.1.1 (a) – (d)). Therefore, during successive analyses to determine the result of the effect of one parameter at a time, particle-particle interactions should theoretically not have had a significant detrimental effect on comparability. Nevertheless, it was decided to test this experimentally.

The previous section, amongst others, gave an indication of the *accuracy* at the lowest solid concentration achievable with the instrument used during this study. However, since only a single analysis was conducted at each concentration, no indication of the effect of hindered settling on *repeatability* was obtained. The potential effect of hindered settling on repeatability

was therefore investigated by comparing repeated analyses of a single 3.85% ($^{v}/_{v}$) Serina filler sample, with that of the same sample diluted with distilled water to 2.0% ($^{v}/_{v}$).

Materials and Methods:

For each sample, 6 analyses were carried out. With each analysis, the cmp of selected particle sizes ranging between 0.2 μm to 30 μm were recorded (Table 4.2.2.3.1 (a) and (b)). After completion of all 6 analyses, the average cmp was calculated for each particle size, as well as the averages for all particle sizes of each analysis.

The stdev of each particle size over all 6 analyses was also calculated, and then the average of the stdevs of all particle sizes were computed. Among the stdevs of each particle size, however, were included those of the particle sizes 0.4 μm and smaller. All of these are already susceptible to Brownian movement. For this reason the average of the stdevs was calculated only for particles larger than 2 μm – the particle size range normally used to compare results during this study. However, to get the complete picture: the average stdevs for only the particles acted on by Brownian movement ($\leq$ 0.4 μm) was also calculated.

It must be mentioned, though, that the cmp at 0.2 μm of the first analysis of the 3.85% ($^{v}/_{v}$) suspension displayed a typical spike in cmp. This normally occurs roughly every fifteen analyses at only one esd. This anomalous cmp value was therefore discarded in the determination of the stdev of 0.2 μm, since the same did not occur at 2.00% ($^{v}/_{v}$). These spikes, occurring now and then, must have been of an instrumental origin since the same sample was used for all analyses.

Lastly, at 30 μm all recorded graphs start at 100% cmp since the 100% adjustment at the beginning of each analysis ensures it. The cmp values of 30 μm will therefore, out of necessity, always have a zero stdev. Hence, for the average of the stdevs calculation the cmp values at 30 μm were not included either.

A further experiment was designed to determine the *difference in cmp* at different particle sizes between the solids contents of 3.85% ($^{v}/_{v}$) and 2.00 % ($^{v}/_{v}$) for three different kaolinite types. The kaolinite types used were Serina filler, Dinkey coater (D_{max} 30 μm), and Amazone coater. One sample of each kaolinite type was made up at 3.85% ($^{v}/_{v}$), soaked for 12 days, and ultrasonicated directly afterwards for the standard 3 min. These samples were then analysed down to 0.2 μm, and the results noted at a number of selected particle sizes. After that, the same samples were diluted with distilled water to 2.00 % ($^{v}/_{v}$), and analysed again.

Table 4.2.2.3.1. Accurately determining particle size distributions at different solid concentrations

The Serina clay sample was dispersed with 1.2% Dispex, followed by 3 min. ultrasonication before the first analysis.

PARTICLE SIZE (µm)	CUMULATIVE MASS % UNDERSIZE Repetitive runs of the same sample 1	2	3	4	5	6	Average cmp	Standard Deviation
0.2	**19.0**	21.0	21.0	21.0	21.0	21.0	21.0	0.00
0.3	28.5	28.0	28.5	29.0	29.0	28.5	28.6	0.38
0.4	33.5	32.5	33.0	33.5	33.0	33.0	33.1	0.34
0.8	43.0	42.5	43.0	43.5	43.5	43.5	43.2	0.37
1	46.0	45.5	46.0	46.5	46.5	46.5	46.2	0.37
2	60.0	59.5	60.0	60.0	60.5	60.0	60.0	0.29
3	70.0	70.0	70.5	70.5	70.5	70.5	70.3	0.24
5	83.0	82.5	83.0	83.5	83.5	83.0	83.1	0.34
10	95.0	94.0	95.0	95.0	95.0	94.0	94.7	0.47
20	99.0	99.0	99.5	99.0	99.5	99.0	99.2	0.24
30	100	100	100	100	100	99.5	99.9	**Av. Stdev ≥ 2 µm: 0.32**
Av.:	61.5	61.3	61.8	62.0	62.0	61.7	61.7	**Stdev of av. cmps: 0.23**
								(Av. Stdev ≤ 0.4 µm : 0.29)

The fist Cumulative Mass % Undersize value of run 1 (namely 19% at 0.2 µm) was much to low and was left out in the calculation of the average particle size and standard deviation for 0.2 µm.

(b) SERINA FILLER, 2.0 % SOLIDS (BY VOLUME)

PARTICLE SIZE (µm)	CUMULATIVE MASS % UNDERSIZE Repetitive runs of the same sample 1	2	3	4	5	6	Average cmp	Standard Deviation	Ave. cmp difference (3.85 solids - 2.0% solids)
0.2	16.0	15.5	16.0	16.5	16.0	15.0	15.8	0.52	5.2
0.3	23.5	23.0	24.0	23.5	23.0	22.5	23.3	0.52	5.3
0.4	29.0	28.5	28.5	28.5	28.5	28.0	28.5	0.32	4.6
0.8	39.5	39.5	39.5	40.0	38.0	39.0	39.3	0.69	3.9
1	43.5	43.5	43.0	43.5	43.0	43.0	43.3	0.27	2.9
2	58.0	57.5	57.5	58.0	57.5	57.5	57.7	0.26	2.3
3	67.5	68.0	68.0	68.5	67.5	68.0	67.9	0.38	2.4
5	81.0	81.0	81.5	81.5	81.5	81.5	81.3	0.26	1.8
10	93.0	94.0	94.0	94.0	93.5	94.0	93.8	0.42	0.9
20	98.5	99.0	98.0	99.0	98.5	99.0	98.7	0.41	0.5
30	100	100	99.0	100	99.0	100	99.6	**Av. Stdev ≥ 2 µm: 0.34**	
Av.:	59.0	59.0	59.0	59.4	58.7	58.9	59.0	**Stdev of av. cmps: 0.19**	
								(Av. Stdev ≤ 0.4 µm: 0.46)	

Table 4.2.2.3.2. Establishing the effect of hindered settling for kaolinite suspensions within workable limits of solid concentration for the Sedigraph 5000D.

The particle size was determined at 3.87 % by volume, whereafter the same sample was diluted with distilled water to 2 % by volume.

SERINA FILLER* (1.2 % DISPEX)			
PARTICLE SIZE (µm)	Cummulative Mass Percentage		
	3.85 % Solids ($^{V}/_{V}$)	2 % Solids ($^{V}/_{V}$)	Cmp difference
0.2	21.0	15.8	5.2
0.3	28.6	23.3	5.3
0.4	33.1	28.5	4.6
0.8	43.2	39.3	3.9
1	46.2	43.3	2.9
2	60.0	57.7	**2.3**
3	70.3	67.9	2.4
5	83.1	81.3	1.8
10	94.7	93.8	0.9
20	99.2	98.7	0.5
30	99.9	99.6	0.3

DINKEY COATER 2 (0.9% DISPEX)			
PARTICLE SIZE (µm)	Cummulative Mass Percentage		
	3.85 % Solids ($^{V}/_{V}$)	2 % Solids ($^{V}/_{V}$)	Cmp difference
0.2	42.5	32.0	10.5
0.3	51.5	43.0	8.5
0.4	57.0	49.5	7.5
0.8	69.0	62.5	6.5
1	73.0	67.0	6.0
2	87.5	82.0	**5.5**
3	94.0	90.0	4.0
5	98.0	96.0	2.0
10	99.5	98.5	1.0
20	100.0	99.5	0.5
30	100.0	100	0.0

AMAZONE (2.0% DISPEX)			
PARTICLE SIZE (µm)	Cummulative Mass Percentage		
	3.85 % Solids ($^{V}/_{V}$)	2 % Solids ($^{V}/_{V}$)	Cmp difference
0.2	72.0	63.5	8.5
0.3	88.0	84.5	3.5
0.4	93.0	90.5	2.5
0.8	97.0	96.0	1.0
1	97.5	96.5	1.0
2	98.5	97.5	**1.0**
3	99.0	98.0	1.0
5	99.0	98.5	0.5
10	99.5	99.0	0.5
20	100.0	99.5	0.5
30	100.0	100	0.0

* The Cumulative Mass Percentage values for Serina filler is the averages of the 6 repetitive runs of the previous sample done respectively at solid contents of 3.85% and 2.0% volume conc. (see Table 5.2.3.2.1.1).

Fig. 4.2.2.3.1 (a)

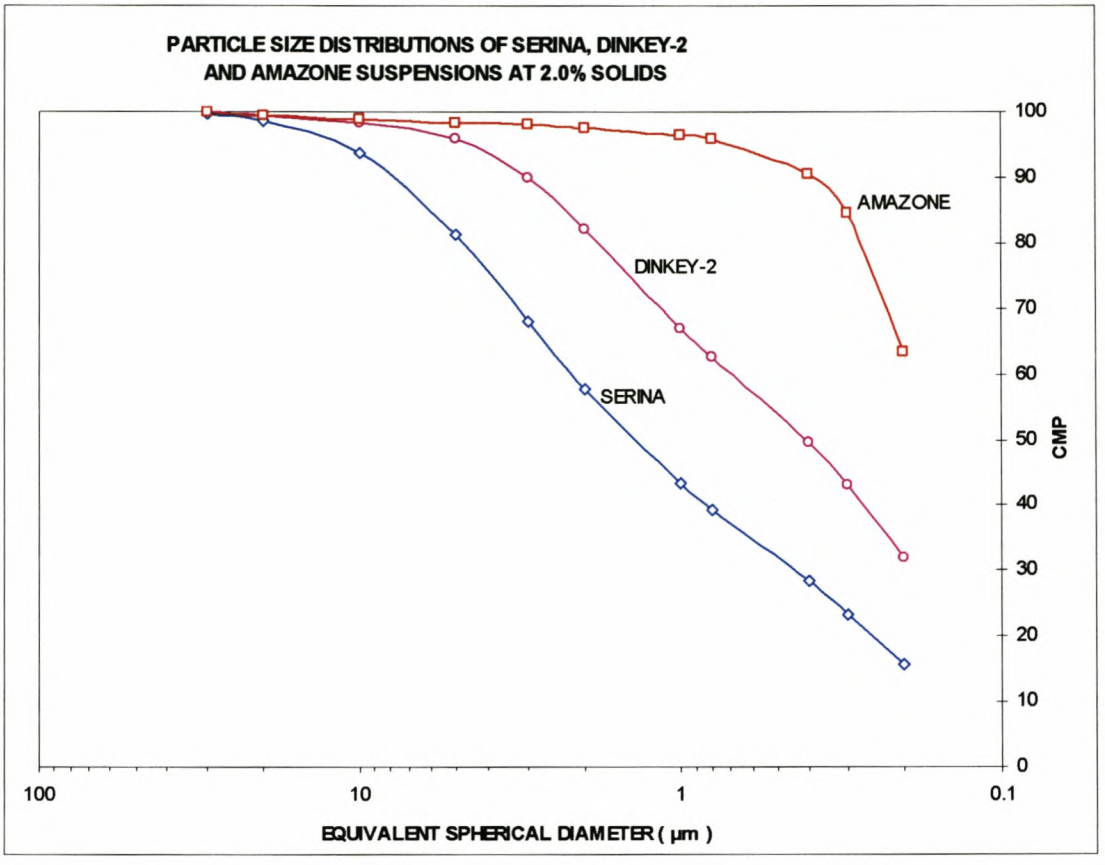
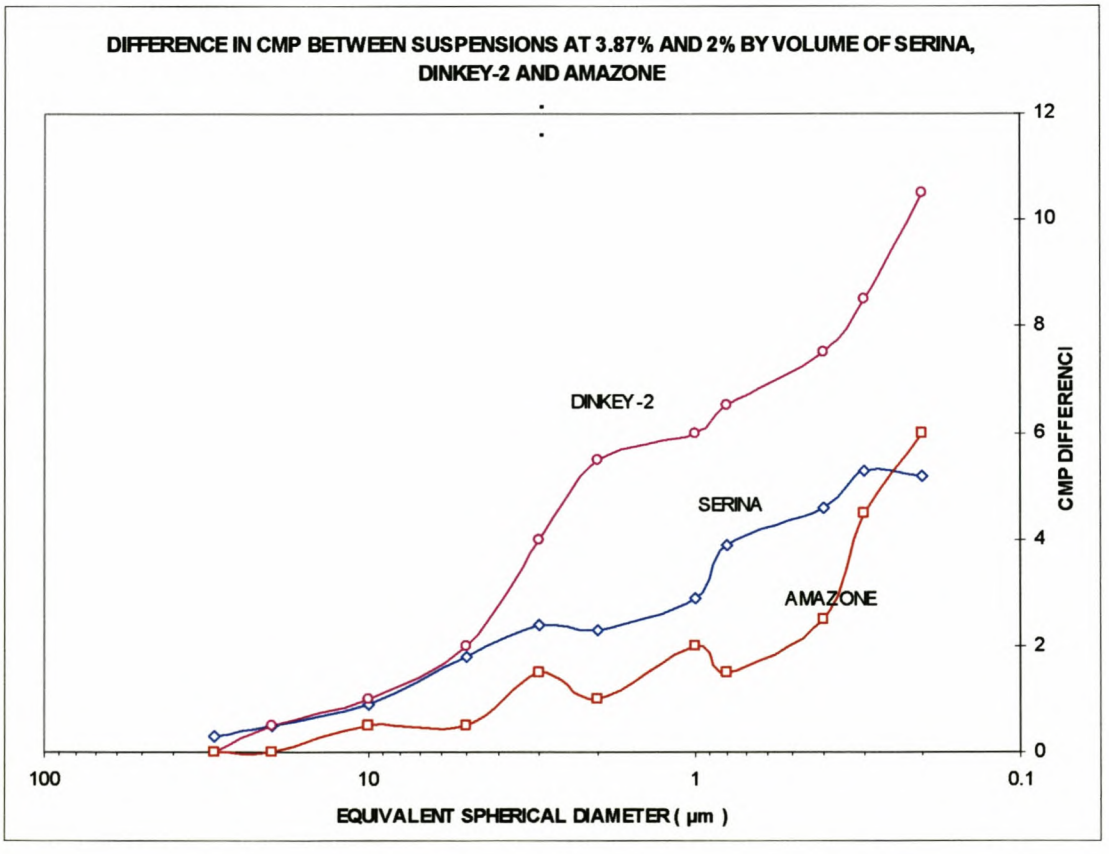


Fig. 4.2.2.3.1 (b)



This second experiment was conducted to examine the effect that solids content will have on each particle size. The question to be answered was: will there still be an increase in settling velocity of particle clusters, as expected for low solid concentrations (section 1.5.2); or had retardation of settling already commenced, as expected for higher volume concentrations (section 1.5.2.1.2). The first scenario would be typified by the development of too low cmp values at the smaller particle sizes, and generally too high cmps at the middle and larger particle sizes. The second scenario will be ushered in by the rise in cmp of all particle sizes.

The results are given in Tables 4.2.2.3.2 (a) and (b), and Figures 4.2.2.3.1 (a) and (b). The graph of Figure 4.2.2.3.1 (a) presents the normal particle size distributions for the three kaolinite types acquired by plotting Table 4.2.2.3.2 (a) and (b) at 2.0% solids content, whereas Fig. 4.2.2.3.1 (b) illustrates the differences in cmp at different particle sizes for each kaolinite type. The latter difference was obtained by subtracting the cmps at the lower solid content from those at the higher solids content.

Results and Discussion:

The stdevs of the samples at the higher solids content (3.85% $^{v}/_{v}$) – as used on the Sedigraph during this study – show that it gave better results in terms of repeatability than when the analysis was performed at the lower solids content (2.0% $^{v}/_{v}$) (Table 4.2.2.3.1 (a) and (b)). For the higher solids content sample this was the case even at the smallest particles sizes ≤ 0.4 µm. The reason for this probably was that the percentage lowering of the transmitted X-ray intensity at the 2.00% volume concentration reached only 23.5%, and not the required minimum of 40% as it should have reached (Table 4.2.2.1.1).

Secondly, for all the kaolinite types, the higher solid concentration samples had increasingly higher cmps towards smaller particle sizes than those with lower solid concentration (Tables 4.2.2.3.2 (a) and (b), and Figures 4.2.2.3.1 (a) and (b)). In the higher concentration samples, therefore, hindered settling increased towards smaller particle sizes. The maximum effect of hindered settling was smallest for Serina, with a 5.2% difference at 0.2 µm; and the largest for Dinkey coater at a 10.5% difference at 0.2 µm.

The results are the opposite of what would have been expected for the combined effect of particle collisions and hindered settling at solid concentrations below 1.0%. At this solid concentration, both these effects cause the increase of settling velocity of particle clusters. This causes lower cmp values at the smallest particle sizes (section 1.5.2). However, with this experiment, the cmp enlarged with decrease in particle size. This indicates that at the 3.85%

volume concentration needed for the instrument used, high concentration hindered settling had already caused a noticeable retardation of settling velocity.

With the higher solids content samples, the tree kaolinite types were affected differently by hindered settling. For Amazone coater, the increase in cmp only become obvious for particles below 5 µm; for particles larger than that, the cmp difference between the two solid concentrations was 0.5% and less. But, for Serina filler and Dinkey coater a difference between higher and lower concentrations already became noticeable at particles smaller than 20 µm. This is probably due to a greater upsurge of displaced suspension liquid for the latter two kaolinite types, since they have greater volumes of larger particles (section 1.5.2.1.2). Hence, smaller particles will be retarded more, leading to increasingly higher cmp values towards smaller esds.

Moreover, the order of magnitude in particle retardation differed between the three latter kaolinite types: Dinkey coater had the largest, followed by Serina filler, and lastly by Amazone coater. The reason for this might be found in dissimilar electro-viscosities for these three kaolinites. It is caused either by a higher Dinkey surface charge per unit area; and/or the conductivity of the Dinkey suspension was lower than those for Serina filler and Amazone coater (see Eq. 1.6.2.1). Both these suspension characteristics will jointly enlarge the electro-viscosities, leading to smaller settling velocities, and therefore to higher cmp values.

Conclusions:

1. When the solids content of the Sedigraph 5000D is increased from 2.00% ($^{v}/_{v}$) to 3.85% ($^{v}/_{v}$), the error due to particle interactions becomes higher the smaller the particle size becomes.
2. In contrast to the last-mentioned effect on *accuracy*, the higher 3.85% ($^{v}/_{v}$) solids content sample had an excellent *repeatability* right down to the smallest particle sizes. It even had better repeatability than the 2.00 % ($^{v}/_{v}$) sample.

   On these grounds, the higher solids content that had to be used throughout this study was in fact preferable.

4.2.2.3.1 Accurately determining the repeatability of the instrument used during this study at its minimum solids content

During the above two series of tests, the cmp was read off from the graph only to the nearest 0.5% with the plastic strip. To get a more accurate indication of the true repeatability

of the instrument used during this study, a further series of successive analyses was performed with a single sample. But this time, the graphs were read off accurate to the nearest 0.1%.

Materials and Methods:

A single Dinkey coater sample was analysed 16 times consecutively. The results was read off at a number of chosen particle sizes, and recorded in Table 4.2.2.3.1.1. Subsequently, the average cmps for all particle sizes of each individual analysis, as well as their stdev over all analyses were calculated. Thereafter the stdev of every particle size over all analyses, and their average was computed. Lastly, the maximum variation in cmp over all analyses for each particle size was determined. Since at the start of every analysis the cmp value at the D_{max} of 30 µm is accurately adjusted to 100%, its stdev and maximum variation were not calculated since it cannot fluctuate.

Lastly, the stdevs of all particle sizes were plotted on Fig. 4.2.2.3.1.1, to give a graphic illustration of the repeatability of the Sedigraph 5000D at its minimum solid concentration of 3.85% ($^{v}/_{v}$).

Results and Discussion:

The stdevs of the recorded particle sizes ranged between 0.16% and 0.27% cmp (Table 4.2.2.3.1.1). The low average value for stdev of ± 0.22 over all particle sizes implies an excellent repeatability for the instrument used during this study. This stdev of ± 0.22 is very close to the accuracy of ± 0.1 at which the graph was read off with the plastic strip in the first place.

The maximum variation in cmp of all particle sizes over all analyses was 1.1% cmp, averaging at 0.8% cmp. This gives a largest error fluctuation of ± 0.55% (± 0.4% on average).

The average cmps of over all the particle sizes of each analysis did not increase significantly over the 15 runs, and its stdev of 0.16 was exceptionally low.

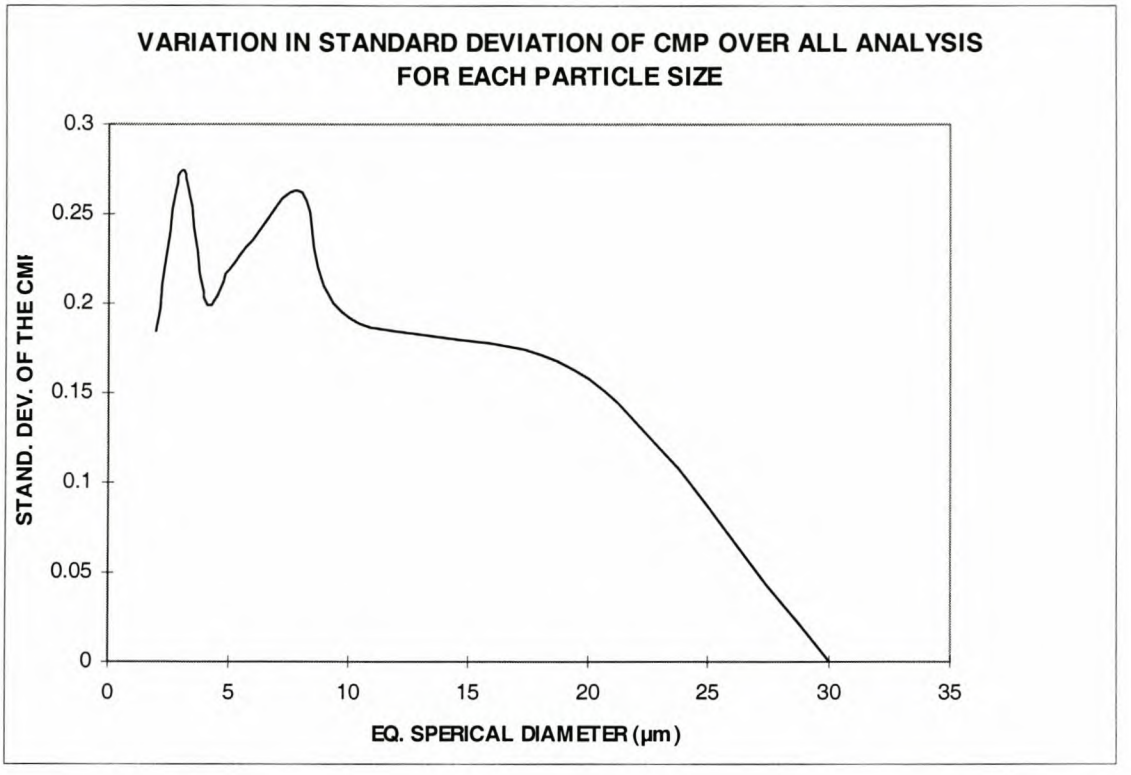
Lastly, Fig. 4.2.2.3.1.1 discloses that the variation in cmp is generally largest at the smaller particle sizes, and that it declines towards the bigger particle sizes.

Table 4.2.2.3.1.1. Accurately determining the reproducibility of the Sedigraph 5000D.

Dinkey coater, Dispex 0.9% (3.87 % solids by volume)

PART. SIZE (µm)	CUMULATIVE MASS PERCENTAGE Repeated analysis of a single Dinkey coater sample Read off from the graph accurate to the nearest 0,1% cmp.															Std. Dev.	Max. cmp variation within part. size class
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15		
2	82.1	82.0	81.8	81.8	81.8	81.4	81.8	81.7	81.9	81.9	82.1	81.9	82.1	82.0	82.0	0.18	0.7
3	90.0	90.2	89.9	89.8	89.5	89.1	89.8	90.0	89.8	89.8	89.8	89.8	90.1	90.2	89.8	0.27	1.1
4	93.9	93.5	93.4	93.1	93.2	93.2	93.5	93.3	93.3	93.4	93.4	93.3	93.5	93.7	93.4	0.20	0.8
5	95.7	95.7	95.3	95.0	95.3	95.1	95.3	95.4	95.3	95.3	95.4	95.4	95.5	95.7	95.7	0.22	0.7
6	96.9	97.1	96.9	96.5	96.8	96.4	96.5	96.8	96.8	96.6	96.9	96.6	97.0	97.0	97.2	0.24	0.8
8	98.3	98.7	98.6	98.2	98.3	97.9	98.0	98.0	98.3	98.0	98.0	97.9	98.5	97.9	98.1	0.26	0.8
10	98.9	99.1	99.1	98.8	98.9	98.5	98.8	98.5	98.7	99.0	98.8	98.7	99.1	98.9	98.8	0.19	0.6
20	100.0	99.9	100.0	100.0	100.0	99.7	100.0	99.5	100.0	100.0	100.0	99.7	100.0	99.8	99.8	0.16	0.5
30	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	Av. Stdev = 2 µm: 0.22	
	94.5	94.5	94.4	94.2	94.2	93.9	94.2	94.2	94.3	94.3	94.3	94.2	94.5	94.4	94.4	Stdev of av. cmps: 0.16	Av.: 0.8 Largest: 1.1

Fig. 4.2.2.3.1.1. Reproducibility of the Sedigraph 5000D at 3.87 % solids by volume.



Conclusions:

1. The instrument used, despite its weakened X-ray intensity, still gave an exceptional repeatability. This is proven by an exceptionally low stdev (0.22%), and a low maximum error fluctuation in cmp (0.55%).

   This is approximately half of the ± 1% error fluctuation reported by the instructions manual of the Sedigraph 5000D. This indicates that the measures taken to keep apparatus-related parameters at bay were successful (see at the start of section 3).

2. A second implication of the exceptionally low average stdev and error fluctuation is the following: variations in the results when a single parameter was changed during this study, was caused only by the change of that single parameter, and not by discrepancies inherent to the material, the instrument, or the methodology. This is confirmed by the very low stdev of 0.16% for the average cmps of all particle sizes during each analysis.

3. The low stdev for the average cmps of all particle sizes during each analysis (0.16%) also proves that the average stdev (0.22%) was not in any way linked to a reduction in particle size due to the mechanical action of re-analysis (shaking, kneading action of pumping, and chopping action of the magnetic stirrer).

4. The general decline in the repeatability towards smaller particle sizes affirms the conclusion of the previous section that hindered settling increases as particles becomes smaller (Tables 4.2.2.3.2 (a) and (b), and Figures 4.2.2.3.1 (a) and (b)).

5. For all kaolinites tested, between 7 min. and 15 min. of ultrasonic treatment was required to reach the second cmp plateau (Fig. 4.1.3.1.1 (a) – (d)). However, in order to save time, 3 min. ultrasonic treatments were used during this study. This was long enough for all kaolinite types to only reach the first cmp plateau value. The above results, obtained with 3 min. ultrasonic treatments, show that this ultrasonic time can be justified by the fact that it produced such good repeatability and reproducibility. All other parameters could therefore be compared safely when using 3 min. ultrasonic treatments. This approach, though, would have affected accuracy somewhat – but not seriously so (Tables 4.1.3.1.1 (a) - (c) and Figures 4.1.3.1.1 (a) - (d)).

4.2.3 Effect of hydrolysis of deflocculants with ageing

The hydrolysis of deflocculants by active clay surfaces increasingly reduces the concentration of free pyrophosphate deflocculant molecules in the suspension liquid over time (section 1.5.6). Hence, ageing of kaolinite suspensions should reduce the accuracy, and perhaps even the reproducibility of particle size analyses.

To investigate whether kaolinite suspensions would become unstable due to the hydrolysis of any of the four deflocculant types, a number of samples dispersed with each deflocculant were aged over a period of 6-months. During this time, the stored samples were repeatedly analysed to check whether they experienced any sharp rise in cmp. The latter would indicate the point of onset of instability due to hydrolysis. With further ageing, subsequent analyses would reveal any increase in the effect of hydrolysis on accuracy and reproducibility. However, if during this long period of soaking ultrasonic treatment was used with every analysis to re-suspend the sediment, de-aggregation could mask a rise in cmp expected to be caused by hydrolysis (section 4.1.3.2.1). To try to prevent this, samples were only shaken to re-suspend them before each analysis.

The possibility also arose that repeated shaking would increasingly dissolve CO_2, and thereby enrich the $CO_3^{=}$ content. Should this happen, it could increasingly have lowered the pH as the multiple analyses proceeded. It was therefore necessary to know whether the potential lowering in the pH could have added to the possible increase in cmp values expected from hydrolysis. Accordingly, the pH of one sample of each deflocculant type was determined

before each of the consecutive analysis.

The experiment to explore the possible onset of instability, due to hydrolysis of deflocculants on active kaolinite surfaces, is described next.

4.2.3.1 Inaccuracy resulting from hydrolysis with ageing

Previously, in section 4.1.3.2.1, we saw that soaking combined with re-sonication reduces the particle size of stored Dinkey filler samples (Tables 4.1.3.2.1.1 (a) – (c)). The current series of experiments will now also present the opportunity to establish whether soaking over such a long period of time, when combined with the mechanical action of multiple shaking and of re-analysis, would increasingly de-aggregate Dinkey coater (D_{max} 30 μm) samples. For this reason only, the cmp below 2 μm was noted with each successive analysis, since potential de-aggregation would be most visible at small particle sizes.

Secondly, the repeated analyses after long periods of storage gave the additional chance to find out whether only shaking of a kaolinite sample was enough to completely re-suspend it after long periods of sedimentation. This part of the test would be to uncover whether the particle size analyses results remained the same over the whole of the 6-month period. Otherwise, after each long period of storage, re-sonication would additionally be necessary, to break up flocks or agglomerates that might have re-formed in the sediment on the bottom of the container.

Materials and Methods:

Six samples of Dinkey coater (D_{max} 30 μm) were made up with each of the deflocculants Calgon, Dispex, Floccotan, and TSP. They were prepared at their optimum deflocculant concentrations, which are: 0.7% for Calgon, 0.5% for TSP, 0.9% for Dispex, and 0.7% for Floccotan.

Each sample received the standard once off 3 min. ultrasonic treatment in an ultrasonic bath. Thereafter each sample was analysed down to 2 μm.

Starting after the first analysis, from that time onwards all the samples were aged over a period of 6 months. Every sample was re-analysed every week, during the first 5 weeks of soaking. With every analysis, each sample was shaken, and afterwards analysed down to 2 μm. The results were inspected to discover whether a sharp rise in cmp indicated the start of instability due to hydrolysis. Thereafter, over the following 14 weeks, the samples were re-shaken and analysed every second week. Finally, over the last six weeks they were re-analysed

after every third week.

Since this experiment would entail 26 repeated analyses combined with 6 months of soaking, it was decided not to re-sonicate the samples before each analysis. Potentially new break-up of softened aggregates could enlarge the cmp, and thereby mask the possible effects of the onset of hydrolysis. For this reason the samples were only shaken by hand until all sediments was re-suspended. Thereafter shaking was continued for an additional 10 sec. to break up the last re-suspended agglomerates.

The results are given in Tables 4.2.3.1.1 (a) to (d). The average cmps below 2 μm were calculated for each set of 6 samples analysed every day, and are displayed graphically in Figures 4.2.3.1.1 (a) and (b). Figure 4.2.3.1.1 (a) is scaled down to supply the more detailed picture, whereas Figure 4.2.3.1.1 (b) is scaled up to give the total picture over the entire six-month period.

The average cmps of each day were then averaged over the whole of the 6 months period (Table 4.2.3.1.1 (d)), and was plotted in Figures 4.2.3.1.1 (a) and (b) as "Av. cmp all samples: ageing + shaking".

Additionally the average cmp of all samples of only the first day was used to represent the cmp < 2 μm for the case without any hydrolysis. This value is also plotted on Figures 4.2.3.1.1 (a) and (d) as the "Correct cmp: no ageing, only shaking". Its line can now be used as the standard against which to compare the rise in cmp of each deflocculant type due to hydrolysis.

Lastly, when the first Calgon and TSP samples become unstable, it was decided to use them to investigate how flocculation develops over time. At that stage, various Calgon and TSP samples were in different stages of instability – some had not flocculated yet. By from then on, recording their cmps at selected particle sizes, spaced over the whole distribution, would demonstrate which particle sizes, if any, are first to start flocculating. This was done from 18 June onwards, on all the occasions left for analyses until the end of the experiment. These results at selected particle sizes of the Calgon and TSP samples are recorded in Table 4.2.3.1.2.

Table 4.2.3.1.1. Determination of the potential effect of hydrolysis of deflocculant molecules due to catalysis by clay surfaces with aging.

The Dinkey coater (D_{max} 30 μm) was used, dispersed either with Calgon, Dispex, Floccotan or TSP deflocculants.

(a) CALGON DEFLOCCULANT (0.7%)

SAMPLE NUMBER	CUMULATIVE MASS PERCENTAGE < 2 μm REPEATED PARTICLE SIZE ANALYSIS OF THE SAME SAMPLE								
	3 min. ultras	No additional ultrasonic treatment, only 60 sek.shaking before each analysis							
		Analysed every other week					Analysed every 2 weeks		
	Date : 19-Feb	Date : 26-Feb	Date : 05-Mar	Date : 12-Mar	Date : 19-Mar	Date : 26-Mar	Date : 10-Apr	Date : 24-Apr	Date : 08-May
1*	82.0	81.5	82.0	82.5	82.0	82.5	82.0	83.0	**95.6**
2	81.5	81.5	81.5	81.5	81.5	82.0	82.0	82.0	82.0
3	81.5	81.0	81.5	81.5	82.0	82.0	81.5	81.5	82.0
4	81.5	81.5	81.5	82.0	81.5	82.0	82.0	81.5	82.0
5	81.5	81.5	81.5	81.5	81.5	82.0	82.0	82.0	82.0
6	81.0	81.5	81.0	82.0	82.0	82.0	81.5	81.5	82.0
Stdev between1 :	0.22	0.22	0.22	0.27	0.27	0.00	0.27	0.27	0.00
Av. cmp this day[1] :	81.40	81.40	81.40	81.70	81.70	82.00	81.80	81.70	82.00
Weeks of soaking:		1	2	3	4	5	7	9	11

CALGON DEFLOCCULANT (0.7%) - CONT.

SAMPLE NUMBER	CUMULATIVE MASS PERCENTAGE < 2 μm REPEATED PARTICLE SIZE ANALYSIS OF THE SAME SAMPLE						STANDARD DEVIATION WITHIN SAMPLES[2]
	Analysed every 2 weeks				Analysed every 3 weeks		
	Date : 21-May	Date : 05-Jun	Date : 18-Jun	Date : 03-Jul	Date : 23-Jul	Date : 14-Aug	
1*	**96.4**						0.35
2	82.0	82.0	**97.5**	**98.5**			0.26
3	82.0	82.0	**92.0**	**98.0**			0.34
4	82.0	82.0	**87.0**	**96.0**			0.26
5	82.0	82.0	**83.0**	**92.0**			0.26
6	82.5	82.0	81.5	**85.5**	**97.2**		0.45 **Av.Stdev. within : 0.32**
Stdev between1 :	0.22	0.00	6.60	5.40			**Av.Stdev. between: 0.20**
Av. cmp this day[1] :	82.10	82.00	**88.20**	**94.00**			**Stdev Ave. Cum. Mass%: 0.26**
Weeks of soaking:	13	15	17	19	22	25	

* The first sample was done afterwards in the same manner as the others in order to measure the change in pH. The cum. mass % was written in the table at the equivalent time periods of samples 2 - 6.

[1] The first sample was not included in this calculation because it was done later to measure the change in pH over the same time period.

[2] Standard deviations whithin samples (excuding the unstable samples, in bold), indicating the variation in particle size before they became unstable.

TABLE 5.2.2.1.1 (b): TSP DEFLOCCULANT (0.5%)

SAMPLE NUMBER	CUMULATIVE MASS PERCENTAGE < 2 µm REPEATED PARTICLE SIZE ANALYSIS OF THE SAME SAMPLE 3 min. ultras. No additional ultrasonic treatment, only 60 sec.shaking before each analysis Analysed every other week Date : 19-Feb	Date : 26-Feb	Date : 05-Mar	Date : 12-Mar	Date : 19-Mar	Analysed every 2 weeks Date : 26-Mar	Date : 10-Apr	Date : 24-Apr	Date : 08-May
1*	82.5	82.0	82.5	82.0	82.5	82.5	82.5	83.0	82.5
2	82.5	81.0	81.5	81.5	82.0	82.0	82.0	82.0	82.5
3	82.5	81.5	82.0	81.5	81.5	82.5	81.5	82.0	82.5
4	82.5	81.5	81.5	81.5	82.0	82.5	82.0	82.0	82.5
5	82.5	81.5	81.5	82.0	82.0	82.0	82.0	82.5	82.0
6	82.0	81.5	82.0	81.5	82.0	82.5	82.0	82.0	83.0
Stdev between1 :	0.22	0.22	0.27	0.22	0.22	0.27	0.22	0.22	0.35
Av. cmp this day[1] :	82.40	81.40	81.70	81.60	81.90	82.30	81.90	82.10	82.50
Weeks of soaking:		1	2	3	4	5	7	9	11

TSP DEFLOCCULANT (0.5%) - CONT.

SAMPLE NUMBER	CUMULATIVE MASS PERCENTAGE < 2 µm REPEATED PARTICLE SIZE ANALYSIS OF THE SAME SAMPLE Analysed every 2 weeks Date : 21-May	Date : 05-Jun	Date : 18-Jun	Date : 03-Jul	Analysed every 3 weeks Date : 23-Jul	Date : 14-Aug	STANDARD DEVIATION WITHIN SAMPLES[2]
1*	82.5	?	**99.0**				0.28
2	83.0	82.5	**84.5**	**88.0**			0.57
3	82.5	83.0	**84.0**	**86.0**			0.54
4	82.5	83.0	83.0	83.0	**96.0**		0.56
5	82.5	82.5	82.5	**87.0**			0.38
6	83.0	**85.5**	**90.8**	**95.0**			0.53
							Av.Stdev. within : 0.52
Stdev between1 :	0.27	1.25	3.36	4.44			**Av.Stdev. between: 0.25**
Av. cmp this day[1] :	82.70	**83.30**	**84.96**	**87.80**	**96.00**		**Stdev Ave. Cum. Mass%: 0.42**
Weeks of soaking:	13	15	17	19	22	25	

* The first sample was done afterwards in the same manner as the others in order to measure the change in pH. The cum. mass % was written in the table at the equivalent time periods of samples 2 - 6.

[1] The first sample was not included in this calculation because it was done later to measure the change in pH over the same time period.

[2] Standard deviations whithin samples (excuding the unstable samples, in bold), indicating the variation in particle size before they became unstable.

TABLE 5.2.2.1.1 (c): DISPEX DEFLOCCULANT (0.9%)

SAMPLE NUMBER	CUMULATIVE MASS PERCENTAGE < 2 µm REPEATED PARTICLE SIZE ANALYSIS OF THE SAME SAMPLE 3 min. ultras.	No additional ultrasonic treatment, only 60 sek.shaking before each analysis Analysed every other week				Analysed every 2 weeks			
	Date : 19-Feb	Date : 26-Feb	Date : 05-Mar	Date : 12-Mar	Date : 19-Mar	Date : 26-Mar	Date : 10-Apr	Date : 24-Apr	Date : 08-May
1*	81.5	82.0	82.0	83.0	82.0	83.0	82.0	83.0	83.0
2	81.5	82.0	82.0	82.0	82.0	82.5	82.0	82.5	82.5
3	81.5	81.5	82.0	82.0	81.5	82.5	82.0	82.0	82.5
4	82.0	82.0	82.0	81.5	82.0	82.5	82.0	82.5	83.0
5	81.5	81.5	82.0	81.5	82.0	82.0	82.0	82.0	82.5
6	81.5	81.5	82.0	81.5	82.0	82.5	81.5	81.5	82.5
Stdev between1 :	0.22	0.27	0.00	0.27	0.22	0.22	0.22	0.42	0.22
Av. cmp this day[1] :	81.60	81.70	82.00	81.70	81.90	82.40	81.90	82.10	82.60
Weeks of soaking:		1	2	3	4	5	7	9	11

DISPEX DEFLOCCULANT (0.9%) - CONT.

SAMPLE NUMBER	CUMULATIVE MASS PERCENTAGE < 2 µm REPEATED PARTICLE SIZE ANALYSIS OF THE SAME SAMPLE Analysed every 2 weeks				Analysed every 3 weeks		STANDARD DEVIATION WITHIN SAMPLES[2]
	Date : 21-May	Date : 05-Jun	Date : 18-Jun	Date : 03-Jul	Date : 23-Jul	Date : 14-Aug	
1*	83.0	82.0	83.0	82.5	83.0	83.5	0.59
2	83.0	82.5	83.0	83.5	83.0	83.5	0.60
3	83.0	83.0	83.0	83.0	83.0	83.0	0.61
4	83.0	82.0	83.0	83.0	83.0	82.5	0.51
5	82.5	82.0	83.0	83.0	82.5	83.0	0.53
6	83.0	82.5	83.5	83.0	83.0	83.0	0.70
							Av.Stdev. within : 0.59
Stdev between1 :	0.22	0.42	0.22	0.22	0.22	0.35	**Av.Stdev. between: 0.23**
Av. cmp this day[1] :	82.90	82.40	83.10	83.10	82.90	83.00	**Stdev Ave. Cum. Mass%: 0.43**
Weeks of soaking:	13	15	17	19	22	25	

* The first sample was done afterwards in the same manner as the others in order to measure the change in pH. The cum. mass % was written in the table at the equivalent time periods of samples 2 - 6.

[1] The first sample was not included in this calculation because it was done later to measure the change in pH over the same time period.

[2] Standard deviations whithin samples (excuding the unstable samples, in bold), indicating the variation in particle size before they became unstable.

TABLE 5.2.2.1.1 (d): FLOCCOTAN DEFLOCCULANT (0.7%)

SAMPLE NUMBER	CUMULATIVE MASS PERCENTAGE < 2 µm REPEATED PARTICLE SIZE ANALYSIS OF THE SAME SAMPLE								
	3 min. ultras.	No additional ultrasonic treatment, only 60 sec.shaking before each analysis							
			Analysed every other week			Analysed every 2 weeks			
	Date : 19-Feb	Date : 26-Feb	Date : 05-Mar	Date : 12-Mar	Date : 19-Mar	Date : 26-Mar	Date : 10-Apr	Date : 24-Apr	Date : 08-May
1*	81.5	81.5	82.0	82.0	82.0	81.5	81.5	82.0	82.0
2	81.5	81.0	81.5	82.0	**83.5**	**84.0**	**84.0**	**84.0**	**84.0**
3	81.0	81.0	82.0	81.5	81.5	82.0	82.0	82.0	82.0
4	81.5	81.0	81.5	82.0	82.0	82.0	82.0	82.0	82.5
5	81.5	81.0	82.0	82.0	81.5	82.0	82.0	82.5	82.0
6	81.5	81.0	81.5	81.5	81.5	82.0	82.0	82.0	82.0
Stdev between1 :	0.25	0.00	0.29	0.29	0.29	0.00	0.00	0.29	0.29
Av. cmp this day[1] :	81.38	81.00	81.75	81.75	81.67	82.00	82.00	82.17	82.17
Av. cmp all samples:	81.70	81.38	81.70	81.70	81.88	82.28	82.00	82.10	82.40
Weeks of soaking:		1	2	3	4	5	7	9	11

FLOCCOTAN DEFLOCCULANT (0.7%) - CONT.

SAMPLE NUMBER	CUMULATIVE MASS PERCENTAGE < 2 µm REPEATED PARTICLE SIZE ANALYSIS OF THE SAME SAMPLE						STANDARD DEVIATION WITHIN SAMPLES[2]
	Analysed every 2 weeks				Analysed every 3 weeks		
	Date : 21-May	Date : 05-Jun	Date : 18-Jun	Date : 03-Jul	Date : 23-Jul	Date : 14-Aug	
1*	82.0	82.0	83.0	81.5	83.0	83.0	0.55
2	**84.0**	**84.0**	**84.5**	**84.5**	**84.5**	**84.0**	0.41
3	82.0	82.5	82.0	82.5	83.0	82.5	0.55
4	82.0	83.0	83.0	83.0	83.0	83.0	0.65
5	82.0	82.5	82.5	83.0	83.0	83.0	0.59
6	82.0	82.5	82.0	82.0	82.5	83.0	0.50
							Av.Stdev. within : 0.54
Stdev between1 :	0.00	0.29	0.50	0.58	0.29	0.00	**Av.Stdev. between: 0.17**
Av. cmp this day[1] :	82.00	82.67	82.50	82.67	82.83	83.00	**Stdev Ave. Cum. Mass%: 0.37**
Av. cmp all samples:	82.53	82.65	**84.77**	**86.98**	**85.31**	**82.94**	**Av.Stdev. Between**
Weeks of soaking:	13	15	17	19	22	25	**all deflocculants.: 0.21**

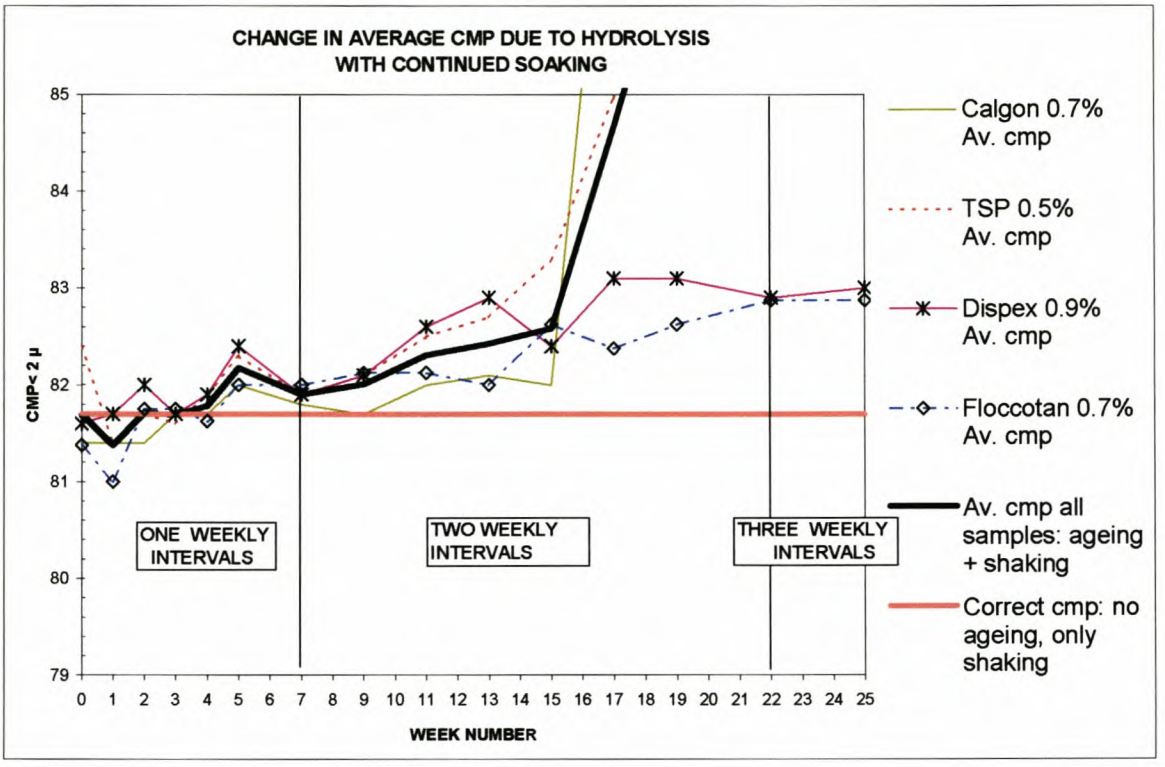
* The first sample was done afterwards in the same manner as the others in order to measure the change in pH. The cum. mass % was written in the table at the equivalent time periods of samples 2 - 6.

[1] The first sample was not included in this calculation because it was done later to measure the change in pH over the same time period.

[2] Standard deviations whithin samples (excuding the unstable samples, in bold), indicating the variation in particle size before they became unstable.

Fig. 4.2.3.1.1. Effect of hydrolysis of deflocculant molecules due to catalysis by clay surfaces with aging.

(a) SCALED DOWN VERSION



(b) SCALED UP VERSION

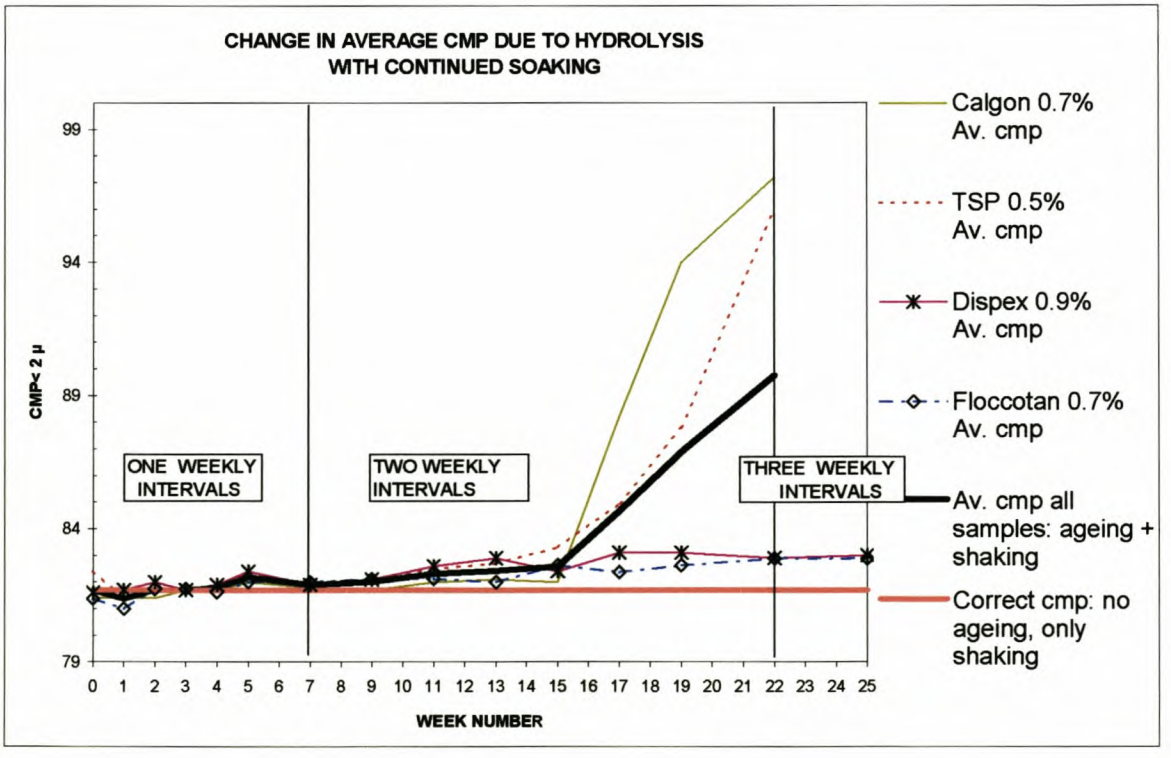


Table 4.2.3.1.2. Experimental particle size distribution: stable vs. unstable samples at three-weekly intervals

The cmps of particle sizes deemed unstable are given in bold.

DATE	DEFLOCCULANT TYPE	SAMPLE NUMBER	Cumulative Mass Percentage at different particle sizes								
			2 μm	3 μm	4 μm	5 μm	6 μm	8 μm	10 μm	20 μm	30 μm
18-Jun	**CALGON (0.7%)**	1*	82.0	90.2	93.9	95.3	96.8	98.4	98.9	100.0	100.0
		2	**97.5**[1]	**98.2**	**98.4**	**98.0**	**98.6**	**98.8**	98.8	99.5	100.0
		3	**92.0**	**92.7**	**94.4**	**95.8**	96.9	98.4	99.0	100.0	100.0
		4	**87.0**	**92.5**	**94.9**	**95.9**	97.0	98.0	98.6	99.8	100.0
		5	**83.0**	90.0	93.8	95.9	97.1	98.5	99.0	99.2	100.0
		6	81.5	88.9	93.9	94.8	96.3	98.0	98.8	100.0	100.0
09-Jul		1	82.0	89.8	93.9	95.6	96.8	98.0	98.4	99.5	100.0
		2	**98.2**	**98.7**	**98.9**	**98.3**	**98.8**	**98.7**	**98.8**	**98.3**	100.0
		3	**98.7**	**98.9**	**98.5**	**98.6**	**98.5**	**99.0**	99.0	99.4	100.0
		4	**98.2**	**98.4**	**98.2**	**97.9**	**98.0**	**98.2**	98.4	99.0	100.0
		5	**97.0**	**97.9**	**97.4**	**97.7**	**98.0**	**98.8**	98.9	100.0	100.0
		6	**90.0**	92.5	94.0	95.1	96.5	98.0	98.6	99.9	100.0
30-Jul		1	**95.6**	**96.2**	**96.8**	**97.8**	**98.1**	**99.1**	**99.5**	99.9	100.0
		2	**98.5**	**98.9**	**99.0**	**98.4**	**98.3**	**98.7**	**98.8**	99.7	100.0
		3	**98.8**	**99.0**	**99.1**	**99.1**	**99.1**	**99.2**	**99.0**	100.0	100.0
		4	**98.7**	**99.0**	**99.0**	**98.8**	**98.8**	**99.2**	**99.1**	99.8	100.0
		5	**99.0**	**99.1**	**99.0**	**99.0**	**99.1**	**99.0**	**99.0**	100.0	100.0
		6	**97.3**	**98.2**	**98.8**	**98.4**	**98.9**	**99.3**	**99.1**	99.8	100.0
			2 μm	3 μm	4 μm	5 μm	6 μm	8 μm	10 μm	20 μm	30 μm
18-Jun	**TSP (0.5%)**	1*	82.5	90.5	94.2	95.9	97.0	98.2	98.8	99.8	100.0
		4	83.0	87.0	93.3	95.1	96.5	98.0	98.9	99.5	100.0
		5	82.5	90.5	94.0	95.6	96.7	98.5	99.0	99.9	100.0
		6	**90.1**	**93.1**	**94.8**	95.9	96.9	98.1	98.6	99.8	100.0
09-Jul		1	82.5	90.3	94.1	95.8	96.9	98.0	98.9	99.5	100.0
		4	**89.3**	**91.8**	94.2	95.9	96.9	98.0	99.0	100.0	100.0
		5	**86.3**	**92.0**	94.5	96.0	96.9	98.0	98.9	99.7	100.0
		6	**97.9**	**98.0**	**97.9**	**98.0**	**98.1**	**99.0**	99.0	100.0	100.0
30-Jul		1	82.5	90.1	93.8	95.3	96.3	98.0	98.7	99.8	100.0
		4	**96.8**	**97.2**	**97.4**	**97.5**	**98.1**	**99.0**	99.0	100.0	100.0
		5	**93.5**	**94.1**	**95.0**	**96.1**	**97.0**	97.9	98.5	99.8	100.0
		6	**98.4**	**98.4**	**98.1**	**98.1**	**98.5**	**98.6**	98.7	99.3	100.0

* After 4 weeks of testing (same sample as used in sample 1 on 19 Mar - see Table 4.2.3.1.1)

[1] Values in bold markedly differ in particle size from that of the stable samples (samples 1, of 18 June).

Results and Discussion:

In Tables 4.2.3.1.1 (a) - (c), and Fig. 4.2.3.1.1 (a) and (b) three distinct phases in cmp change can be distinguished: each with a sharper rise than the previous one. The cmp change at the end of each phase is caused by two distinct mechanisms *viz.* de-aggregation and hydrolysis. The indicators of each of these mechanisms are discussed next, along with the data

relevant to each.

For the first 4 weeks, the ***average cmp for all samples*** of the original samples 2 to 6 stayed virtually the same for all deflocculants. At the second analysis, though, the average cmp for all samples dropped with about 0.4%, because of a lowering in cmp of both the second TSP (-1%) and Floccotan samples (-0.5%). This, however, is within the normal fluctuation to be expected with repeated analysis of the same sample. Experience showed that when re-analysing the same sample with the apparatus used, then there is an unexplained 0.5% – 1.0% change in cmp at roughly every 15 analyses.

The observed constant *average cmp for all samples* during the first 4 weeks signifies that soaking and shaking without re-sonication does not soften aggregates enough to benefit the de-aggregation of Dinkey coater (D_{max} 30 µm) samples.

After 5 weeks of storage, however, the average cmp for all samples gradually and continuously starts to rise. This indicates that after 5 weeks of soaking, the aggregates are softened enough that de-aggregation now starts to increase the cmp below 2 µm. However, it is only from 11 weeks onwards that the average rise in cmp passes beyond a 0.5% above the correct cmp without ageing. A rise in cmp larger than 0.5% is considered as inaccuracy.

The most likely mechanism that brings about the inferred de-aggregation due to soaking and repeated analyses, is the shaking needed to re-suspend the samples. During successive analyses, however, the mechanical action of the apparatus itself might also contribute to the breaking up of agglomerates. This can firstly be caused by the kneading action of the peristaltic pump. Pumping is performed twice during each re-analysis: first during the 100% adjustments, and then again after each analysis, to re-suspend the sediment on the bottom of the sample cell. Additionally, during each re-analysis, the chopping action of the magnetic stirrer might add to the break-up of aggregates.

Tables 4.2.3.1.1 (a) - (c), and Fig. 4.2.3.1.1 (a) and (b) furthermore show that from week 15 onwards the *average cmp for all samples* started to rise sharply above the correct cmp value. This was mainly due to the sudden increase in cmp of both the TSP and Calgon samples onwards, respectively, from week 13 and 15. This sudden increase in cmp is attributed mainly to an early development of instability – de-aggregation should also have contributed, but probably was not the main cause for it. With the foregoing de-aggregation, the *amount* of smaller, slow moving particles was increased, thus increasing the cmp below 2 µm. But after the onset of the early development of instability, the formation of a continuous matrix

inhibited the sedimentation rate, which lead to the observed sharp increase in the cmp below 2 μm. Instability was proven as the main cause for this by a simultaneous, and sudden appearance of visual signs of instability in the plastic storage bottles. Thereafter, these visual signs grew in substance, concurrent with the continued sharp rise in cmp.

The visual signs of the onset of instability in the storage bottles were the following:

- After 2 weeks of standing, the clay/water interface suddenly dropped from about $^1/_3$ below the water level, to $^2/_3$ below. In addition, the interface became sharp, where usually it has a hazy upward weakening in particle concentration. The latter is caused by the progressive increase in the sedimentation distance as particle sizes become larger with greater depth below the interface. However, with the onset of instability particles start to flocculate. This should destroy the concentration graduation at the top of the suspension.
- The sample suspension after being shaken, for the fist time started to stick to the insides of its storage bottle. The suspension layer covering the inside typically exhibited small rivulet-shaped streaks of clean bottle surface. This is caused when water, running from the thick suspension sticking to the walls, partially washes it away along curving, mm-sized waterways.
- The more the samples became unstable thereafter, the easier it became to re-suspend all sediments from the bottom of the storage bottles through shaking. Stable samples of Calgon took 10 sec. to completely re-suspend; stable TSP samples took 40 sec., and stable samples of both Dispex and Floccotan took 50 sec. Simultaneous with these three signs, the analyses results exhibit its first notable rise in cmp.

Directly after the onset of instability, the plotter-graph will still seems like that of a normal result, but will inadvertently be inaccurate. Therefore, if the above visual signs in the storage bottles are not interpreted correctly, the inaccuracy will stay unnoticed.

When suspensions of Calgon and TSP eventually reached *total instability*, it took only one or two shakes to clear the bottom of the sample storage bottle of all sediments. At this stage, the instability also becomes noticeable on the Sedigraph plotter graph. When a Dinkey coater (D_{max} 30 μm) suspension is stable, its graph fluctuates with only ± 0.8% cmp, and its cmp below 2 μm is already at 81.5% cmp. But, when *total instability* is reached, the graph becomes very irregular, and stays at 99% cmp up to the smallest particle sizes.

The reason why the cmp remains at 99% is that at total instability, all particle sizes

flocculates into one large flock (section 4.1.2.1). Hence, there is no settling of single flocks. This results in a constant sample concentration, right through the whole matrix. Hence, the cmp stay at 99% as the X-ray beam scans the sample cell from bottom where the largest particles should have been registered, to the top where the smallest particles should have been registered.

When the average cmp of ***each separate deflocculant type*** are investigated, the following pattern can be observed (Table 4.2.3.1.1 (a) and Fig. 4.2.3.1.1 (a)):

With the Calgon samples, the average cmp for all its samples stayed essentially the same for the first 2 weeks of soaking. Then, over the next 3 weeks it rose with 0.6%. Thereafter, over the next 10 weeks (up to week 15), it eventually stabilised at around 82%. This relatively slight rise over the whole of this period is interpreted as being produced by a small amount of de-aggregation. Shaking, along with the two mechanical actions of the analysis itself, should be the cause of this. Calgon therefore only slightly assisted the de-aggregation of Dinkey during the first 15 weeks of soaking.

The cmp values of the TSP samples exhibited more fluctuations than with Calgon. For the first 9 weeks the TSP samples, on average, stayed within acceptable limits of accuracy and reproducibility. However, from week 9 to week 15 there was a substantial rise in cmp. This must also be ascribed to de-aggregation, since there were no visual signs of instability in the storage bottles. It was a more substantial rise in cmp than was the case with Calgon. Hence, TSP deflocculant can be regarded as slightly more supportive to de-aggregation than Calgon.

However, after 13 and 15 weeks of soaking for TSP and Calgon suspensions, respectively, the first *visual* signs of instability started to appear in the storage bottles. From these dates onwards, an accompanying sharp rise in cmp became apparent during all the following analyses. This stronger cmp rise is therefore also regarded as being caused by instability due to hydrolysis.

Dispex and Floccotan samples, on the other hand, never became unstable – even after a full 6 months of storage (Tables 4.2.3.1.1 (c) – (d), and Fig. 4.2.3.1.1 (a)). Contrary to Calgon and TSP, Dispex and Floccotan had neither the typical sharp cmp rise, nor any visual signs of instability in storage bottles. Dispex and Floccotan therefore are not hydrolysed with storage of up to 6 months.

However, when studying the Dispex and Floccotan samples more closely, one also observes a small, gradual rise in cmp form start to finish. Over the full 6-month period, the

cmp rose only 1.4% and 1.6% for Floccotan and Dispex, respectively. As with TSP, it started after 5 weeks of soaking and re-analysis. This gradual rise in cmp with Dispex and Floccotan samples is also interpreted as de-aggregation.

The first rise in cmp that is large enough to be viewed as inaccuracy occurred for Dispex after 9 weeks, and for Floccotan after 13 weeks. Due to the absence of visible signs of instability in the sample bottles, the second bigger rise in cmp can be interpreted as being originated by enhanced aggregate break-up. Dispex was already proven the best deflocculant for dispersing kaolinite samples, and as the best benefactor to de-aggregation when preceded by short periods of soaking (section 4.1.2.1). Similarly here, during extended periods of soaking, Dispex once again performed best of all deflocculants in assisting de-aggregation.

To, in conclusion, establish the order of flocculation, the results in Table 4.2.3.1.2 is examined. In order to identify which particle size is first to be affected as instability proceeds, the sample 1 of Calgon on June 18 was used as a standard to which any change in cmp could be detected in the other samples. Up to that date, this sample had not shown any visual first signs of instability in its sample bottle. For TSP sample 1, as well as samples 4 and 5 of June 18 served the same purpose due to the same reason.

The pattern of the results discloses that when instability starts to set in, then the smallest particle sizes are the first to display an increase in cmp (sample 5 of Calgon and sample 6 of TSP on June 18). Evidently, the smallest esds appear to be the first to which flocks are added. If one in Table 4.2.3.1.2 follow the cmp values of a specific sample as instability progresses over time: you discovers that larger and larger particle sizes, one after the other, starts to exhibit a higher cmp. Ultimately, at total instability, the cmp of all particle sizes reaches a more or less 99% apparent cmp. In contrast, the cmp < 2 μm of the stable case is at approximately 81.7%, and the rest of its esds are between that value and the 100% cmp value at the D_{max} of 30 μm.

A feasible explanation why increasingly larger particle sizes become modified as instability progresses is that flock sizes grow as time passes. Thus, one after the other, the cmp of larger, and larger particle sizes gets affected. This growth in flock size alone, though, is not the full explanation for the above pattern. It should be kept in mind that a clay flock must be much lighter than the solid particles it consists of. It probably includes so much water that its density is closer to the density of water than the density of the single particles it consists of. Consequently, the density difference between the flock and that of water (r_l - r_s) is so small that the flock's sedimentation velocity (U_{St}) becomes close to zero (see Stokes' Law, Eq.

1.4.1.1). New flocks therefore sink down so slowly that they will not be measured at the same particle sizes as their actual flock sizes.

Flocks, being lighter, will actually settle at the same velocity as much smaller particles. As a consequence, the first flocks to form would only enlarge the cmps of smaller particle sizes. If this were not the case, then higher esds would have registered the first rise in cmp at the onset of instability. As flock sizes grow with time, however, their settling velocities will likewise be enhanced; and larger and larger particle sizes will increasingly be affected.

Conclusions:

1. When an extended series of analyses must be performed, the samples must be sonicated once off, after a preceding period of soaking. To insure accuracy and reproducibility the soaking needs only be done overnight (Table 4.1.3.2.1).
2. Dinkey coater samples, when dispersed with Calgon and TSP, should not be stored for more than 9 weeks or 15 weeks, respectively, before analysis is conducted. When soaked for a longer duration, then, apart from enlarging their de-aggregation above unacceptable levels, they also start to become unstable due to hydrolysis of the deflocculant molecules. For this reason analyses with Calgon and TSP beyond these storage times can unknowingly cause inaccurate results.

   However, with Dispex and Floccotan there is no onset of instability due to hydrolysis. However, with long storage times (over 9 weeks for Dispex and over 13 weeks for Floccotan) a smaller but significant rise in cmp is brought about. This rise is due to de-agglomeration, effected by repeated shaking and re-analysis.
3. With extended storage, followed by re-analysis, the samples do not need to be ultrasonicated again: only shaking is enough to completely re-suspend the deposited kaolinite, and to secure very good repeatability.
4. Taking in to account all the above: when various samples must be analysed over a long period of time, they can all be made up together, and soaked for up to 9 weeks. Just before the first analysis: all samples must be ultrasonicated one after the other. When an ultrasonic bath is used, then preceding soaking (at least overnight) to first soften aggregates/agglomerates, is a prerequisite (affirm the need for this in Table 4.1.3.2.1.1). For all samples, though, ultrasonic treatment must be performed after the same duration of soaking and with the same ultrasonic time, to produce the same amount of aggregate/ agglomerate break-up for each individual sample. Otherwise, reproducibility will be

sacrificed.

Thereafter, over the next few days, all particle size analyses can be completed without compromising anything on accuracy or reproducibility. However, only shaking to re-suspend the sediment of larger particles should precede each re-analysis. Re-sonication will undermine reproducibility.

5. As soon as visual signs of the onset of instability appear in sample storage holders, such samples must be discarded. Without recognising these signs, the beginning stages of instability cannot be distinguished from stable ones only by using the particle size analysis results themselves. In such cases, inaccurate results will unknowingly be accepted as valid.
6. With Dinkey coater samples the order of efficiency of the four deflocculants to assist de-aggregation (due to repeated shaking and re-analysis) is the following: Dispex is best in promoting de-aggregation, followed closely by TSP and Floccotan, with Calgon a bit further back (see Fig. 4.2.3.1.1 (a)).
7. Previously was seen that of all the kaolinites used during this study, Dinkey coater samples were most easily de-aggregated by re-sonication (Table 4.1.3.2.1.1 (a) – (c)). It therefore follows that the much lower energy of shaking and the mechanical action of re-analysis are not expected to de-aggregate any of the other kaolinites more than was the case with Dinkey coater during this experiment.

   On these grounds, with all the other kaolinite types re-analysis of samples can safely be conducted for up to 9 weeks – with only shaking to re-suspend them – without compromising their accuracy or repeatability.
8. When instability begins to take effect, the accuracy of the smallest particle sizes is affected first. Thereafter, as flocculation advances over time, the cmp of larger and larger particles begins to become inaccurate. This suggests that the density of flocks is much smaller than the particles along which they are measured during the sedimentary methods of particle size analysis. Therefore, the flock sizes are in reality much bigger than the esds at which they are registered.

4.2.3.2 Repeatability and reproducibility with ageing

The stdevs *between* the different samples of *each specific day* were also calculated in Tables 4.2.3.1.1 (a) – (e). This was done to obtain an indication of the *reproducibility* of each deflocculant *for each day of analyses*.

A few stdevs were also calculated over the 2 weeks period before the onset of instability.

This was used to demonstrate the effect on repeatability and reproducibility of de-aggregation only. This was the period before hydrolysis of the deflocculants could reduce the stability of the suspensions. It would identify the deflocculant that caused the most de-aggregation when analyses of a single sample need to be repeated over a long period of time.

First, to be calculated, over the period before instability started, were the averages of the already mentioned stdevs *between* different samples of each specific day. Secondly, the stdev over the period before instability of the averages in cmp of the different samples of each day was obtained. The latter two stdev values were secured to get an indication of how the *reproducibility* of each deflocculant was affected by de-aggregation during the period of soaking before instability started (Table 4.2.3.1.1 (a) - (c), last column).

In addition were calculated the stdevs *within* each individual sample for all its analyses over the period before instability. They are and recorded in Table 4.2.3.1.1 (a) - (c), in the last column. In conclusion, the average for these stdevs *within* individual samples were computed. Both the latter two stdev values were obtained to demonstrate how the *repeatability* of each individual sample was affected by de-aggregation only.

Results and Discussion:

The averages of the stdevs *between* the different samples analysed on the same day differ from each other with more or less equal intervals. The stdevs for Floccotan, Calgon, Dispex, and TSP samples are 0.17, 0.20, 0.23, and 0.25, respectively (Tables 4.2.3.1.1 (a) - (c)). The *average stdev between* different samples for all four deflocculants is 0.21 (Tables 4.2.3.1.1 (c), last column). This firstly points to a very good *reproducibility* between the different Dinkey coater samples analysed on a single day – indicating very homogeneous samples for this kaolinite.

When next inspecting the average stdevs *within* samples, as well as the stdevs of the average cmps, they both signifies that Calgon gave the better results regarding repeatability when samples are analysed many times over. With Calgon the stdev *within* samples and the stdev of the *average cmps* are 0.32 and 0.26, respectively. For the other deflocculants, Floccotan samples had a 0.54 stdevs *within* samples and a 0.37 stdev of the average cmps. For TSP, it was very close to these at 0.52 and 0.42, respectively. Similarly, for Dispex it was 0.59 and 0.43, respectively. Hence, the order in terms of *repeatability* is from best to least good: Calgon, followed by Floccotan, then TSP, and lastly Dispex. The last three had more or less equal repeatability – but although falling somewhat behind Calgon, they still had acceptable

repeatability.

Conclusions:

1. When samples are stored for up to 13 weeks, combined with repeated shaking and analysis, the order of *repeatability* from best to least best is: samples deflocculated with Calgon, followed in close order a bit further back by Floccotan, TSP, and Dispex.

   For best *reproducibility* between different samples, the order was fairly close: Floccotan followed by Calgon, Dispex, and lastly TSP. Ironically Calgon, the deflocculant that gave worst performance in stability over a very long storage period, gave the best results in repeatability as well as reproducibility over the first 3 months of storage (this is storage up to 2 weeks before the first sample gave the first signs of instability).

2. The Dinkey coater samples used during this study were very homogeneous, and consequently gave very good *reproducibility*. This is proven by its very low average stdev between different samples of only 0.21 (combined for all the deflocculant types).

   This indicates that when with Dinkey coater only one chosen parameter is intentionally varied, any change in cmp during such comparative analysis can be ascribed to that parameter only.

4.2.3.3 The effect of a change in pH with ageing on accuracy and reproducibility

During this hydrolysis experiment, only 5 Dinkey coater samples were originally aged with each deflocculant type, and frequently re-analysed. After a number of analyses, though, when the cmps started to rise, the idea developed that a third cause may also contribute to the rise in cmp, *viz.* a lowering in pH with shaking (section 4.1.2.2). Accordingly, an extra sample was at that stage made up for each deflocculant. In addition to particle size analysis on the extra sample, additional pH analyses were performed to verify whether a notable alteration in pH would coincide with the observed increase in cmp.

Materials and Methods:

The cmp results of the extra samples are also given in Table 4.2.3.1.1 (a) - (c)). They are labelled as sample 1.

To be comparable with the other samples, the extra samples were analysed at the same schedule, and under the same experimental conditions as the first 5 samples. The extra samples were not analysed on its dates in Table 4.2.3.1.1 (a) - (c) – to more easily compare results, their cmps were placed in the tables from day one onwards.

Table 4.2.3.3.1. Change in pH due to soaking and shaking of Dinkey coater samples with Calgon, Dispex, Floccotan and TSP deflocculants over a 6 month period

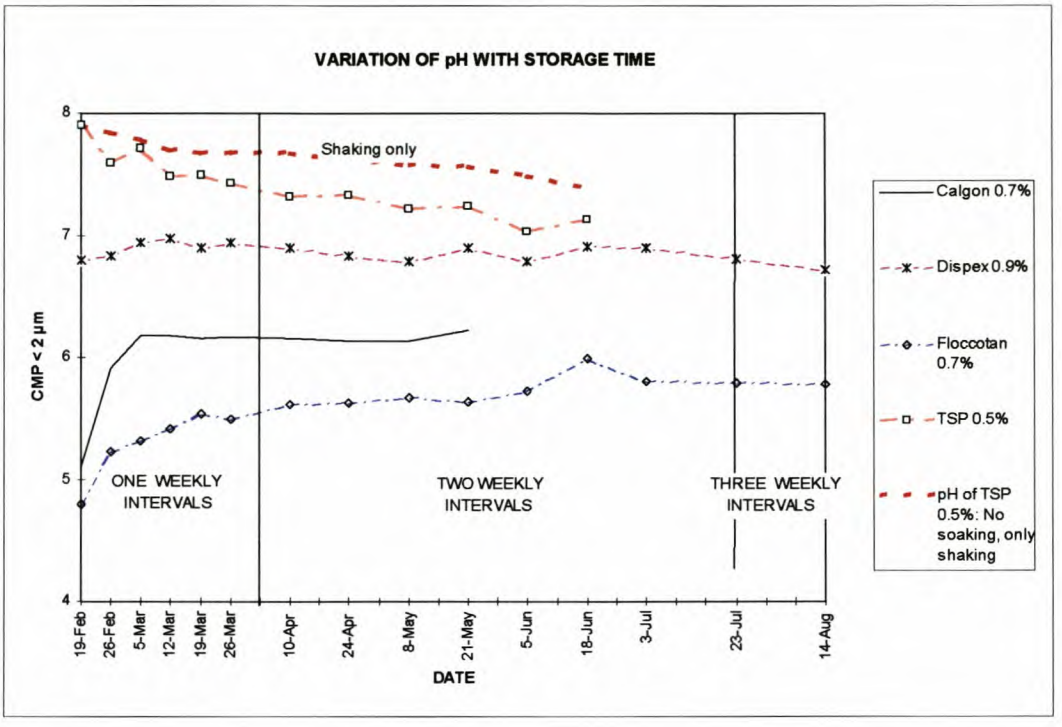
DISPERSANT TYPE	SAMPLE pH SAME DINKEY 2 SAMPLES					
	3 min. ultras.	No additional ultrasonic treatment: only 60 sec. shaking before each analysis Analysed every other week				
	Date : 19-Feb	Date : 26-Feb	Date : 05-Mar	Date : 12-Mar	Date : 19-Mar	Date : 26-Mar
CALGON	5.10	5.91	6.18	6.18	6.16	6.17
DISPEX	6.80	6.83	6.94	6.97	6.89	6.94
FLOCCOTAN	4.80	5.23	5.32	5.41	5.54	5.49
TSP	7.90	7.59	7.71	7.48	7.49	7.42

[1]The cmp values in bold marks the onset of instability of the Calgon and TSP samples.

Table 4.2.3.3.1 continued

SAMPLE pH SAME DINKEY 2 SAMPLES No additional ultrasonic treatment, only 60 sec. shaking before each analysis									STDEV
Analysed every 2 weeks							Analysed every 3 weeks		
Date : 10-Apr	Date : 24-Apr	Date : 08-May	Date : 21-May	Date : 05-Jun	Date : 18-Jun	Date : 03-Jul	Date : 23-Jul	Date : 14-Aug	
6.15	6.13	6.13	6.22	Terminate pH tests because the sample too unstable for particle size analysis.					0.39
6.90	6.83	6.78	6.89	6.79	6.91	6.90	-	6.72	0.07
5.61	5.62	5.67	5.63	5.72	5.99	5.80	-	5.78	0.29
7.31	7.33	7.22	7.24	7.03	7.13	Terminate pH tests because the sample too unstable for particle size analysis.			0.25

Fig. 4.2.3.3.1. The change in pH due to continued soaking and repeated shaking over a 6 month period



Only samples 2 - 5 were used to calculate the averages and stdevs in Table 4.2.3.1.1 (a) - (c). To be on the safe side, the cmp values of the extra samples were left out for this purpose. The reason was that with repeated pH analyses over time, the cumulative effect of possible H_2NO_3 seepage from the pH electrode could have modified the results. This might have been the cause for the Calgon sample 1 reaching instability much earlier than the original samples.

All samples 1, along with the pH meter and the calibration buffer solutions, were placed beforehand in the temperature-controlled room. In this way, they could stabilise overnight to the same temperature. Furthermore, using the method of Rowell (1994), all pH determinations were completed just before the start of each particle size analysis. This would likewise insure that the samples were at the same temperature as that of the pH electrode. If the pH was determined *after* the analysis, the sample temperature would have been between 10 °C to 15 °C higher than that of the pH meter and electrode. Then, the pH meter would have to be re-calibrated to the increasing sample temperature after every analysis. So, completing the pH measurements before the analysis, rather than after it, saved time.

The changes in pH for the four different deflocculants are given in Table 4.2.3.3.1, and plotted on Fig. 4.2.3.3.1.

Finally, there was also the question whether repeated shaking did actually cause the

observed change in pH, or was it in some way related to the long storage time, spaced over 6 months? To establish a potential relationship between the time-factor, the change in the pH, and the change in cmp: one last experiment was devised. For this an extra TSP sample was made up at the same TSP concentration (0.5%), and using same sample preparation as the one above.

The extra TSP sample was shaken 12 times consecutively, at equal durations (60 sec.). In-between each shaking the extra TSP sample was analysed for both cmp and pH. Every cmp measurement was completed directly after the other – all over the course of one day. The pH was again measured directly before each particle size analysis. Preceding each pH measurement, the pH electrode was re-calibrated to the temperature of the sample – which rose as the Sedigraph heated up.

The pH and cmp results for the extra TSP sample are recorded in Table 4.2.3.3.2. The change in pH is also recorded in Fig. 4.2.3.3.2, along with the already discussed change in pH for the 6-month TSP sample. The curve of this extra sample represents 12 analyses completed in only one day. But with each separate run, the change of its pH was plotted to correspond with the date of the matching runs of the other pH samples (which was of course conducted over the space of 6 months). This was done to allow an easy comparison of the pH changes of the two samples for each matching re-shaking.

Results and Discussion:

The Calgon and Floccotan samples that were re-analysed over the period of 6 months had lower start pH values (5.10 and 4.80) than Dispex and TSP (6.80 and 7.90) (Table 4.2.3.3.1 and Fig. 4.2.3.3.1).

Within the first 2-4 weeks the pH of Calgon, Floccotan, and Dispex rose, and thereafter stayed more or less constant for the remainder of the time. Of these, Calgon had the largest increase in pH of 1.08; Floccotan had an in-between rise in pH of 0.74, and Dispex the smallest rise of 0.17. In contrast to the latter three deflocculants, TSP had the highest pH at the start; thereafter it showed no rise, but only a continued and gradual *lowering* of pH.

In conclusion, with continued shaking, both the TSP samples underwent a lowering in pH (Table 4.2.3.3.2 and Fig. 4.2.3.3.2). However, the long storage time appears to have caused a slightly greater pH change in the 6 months TSP sample.

Table 4.2.3.3.2. Change in sample pH and cmp < 2μm of a single Dinkey sample, with TSP deflocculant, and repeated 60 sec. shaking - all completed within one day.

The analysis followed directly one upon the other, and was completed in one day.

Particle size analysis was done after each shaking. It was followed by pH measurement directly afterwards - with the pH electrode calibrated at the temperature of the sample.

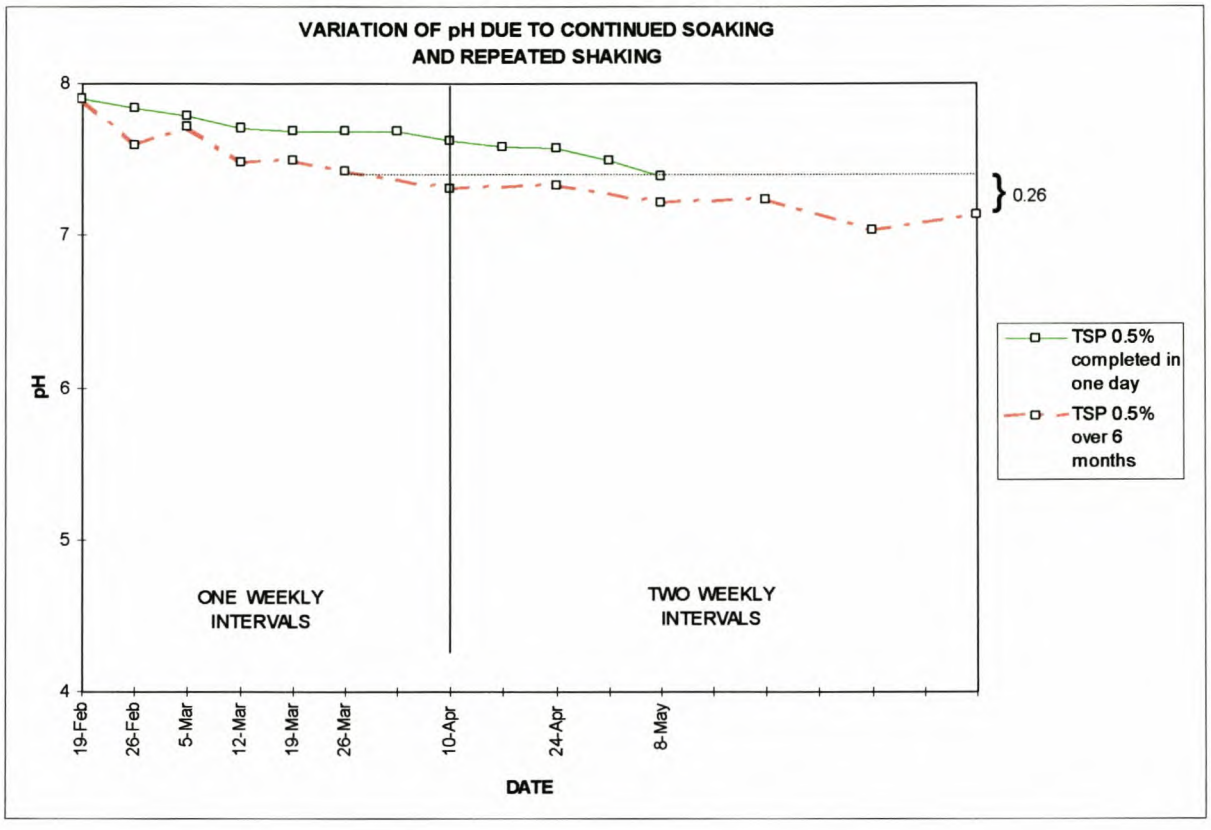
TSP DISPERSANT (0.5%)

SAMPLE PARAMETER	**CHANGE IN IN BOTH PARTICLE SIZE AND SAMPLE pH.** SAME DINKEY SAMPLE					
	3 min. ultras.	No additional ultrasonic treatment: only 60 sec.shaking before each analysis				
	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
CMP < 2μm	82.00	82.00	82.00	82.00	82.00	82.00
Sample pH	7.90	7.84	7.79	7.70	7.68	7.68

Table 4.2.3.3.2 (continued)

CHANGE IN IN BOTH PARTICLE SIZE AND SAMPLE pH. SAME DINKEY SAMPLE No additional ultrasonic treatment: only 60 sek.shaking before each analysis						**AVE.**	**STDEV**
Run 7	Run 8	Run 9	Run 10	Run 11	Run 12		
82.50	82.00	82.00	82.00	82.50	82.50	82.125	0.23
7.68	7.62	7.58	7.57	7.49	7.39	7.66	0.14

Fig. 4.2.3.3.2. Change in pH due to soaking and repeated shaking over 6 months vs. repaeted shaking during one day only



Conclusions:

1. When repeatedly shaken, a pH change occurs for Dinkey coater when dispersed with all four deflocculant types.
2. The fear that the production of H_2CO_3 through repeated shakings could create an increase in acidity was unfounded. With repeated shaking, three of the four samples actually became more alkaline (Dispex, Calgon, and Floccotan).
3. No marked change in pH preceded the onset of instability. Therefore, the change in pH due to shaking, combined with extended storage, could not have caused the onset of instability of the Calgon and TSP suspensions. Instability of the Dinkey coater suspensions must rather be ascribed to hydrolysis of the deflocculant molecules, which resulted over extended storage time from catalysis by the highly charged clay surfaces.
4. Since both TSP samples experienced a lowering in pH, it suggests that the main contribution to pH change, above that of the time factor, was repeated shaking. The reason is that the change in pH was virtually alike for the two TSP samples – despite their greatly

dissimilar soaking times, which practically differed by 6 months.

5. The one-day TSP sample, which was shaken and analysed 12x consecutively in one day, showed no change in particle size distribution (Tables 4.2.3.1.1 (a) – (e)). This verifies the conclusion of the previous section that the gradual rise in cmp below 2 μm of the other samples – stored and re-analysed over a period of 6 months – was mainly caused by the softening of aggregates with extended soaking.
6. The reason why shaking generally changed the pH to slightly higher values is unclear. Firstly, the two TSP suspensions became more acidic with shaking, whereas the suspensions of the other three deflocculants became more alkaline. Equally unclear is why, with long storage, the pH change was more pronounced.

Recommendations for further study:

1. The above results do not conclusively prove the supposition that hydrolysis of Calgon and TSP was the reason for the observed instability of Dinkey coater suspensions. Therefore, it is suggested to again soak these samples until the first signs of instability appear. Thereafter, repeatedly investigate the deflocculant polymer structures in both suspension and supernatant of each successive particle size analysis. Check whether these deflocculants had undergone any chemical changes. Also, determine the deflocculant concentrations at the same intervals, to keep track of its conceivable reduction – a further proof of hydrolysis.
2. The observed enlargement in cmp of one particle size after the other as time progressed is also in itself no proof that this was caused by lighter flocks, growing in size (Table 4.2.3.1.2). It is therefore suggested that, when noticing the first signs of an increase in cmp, to also examine such a suspension microscopically. To accomplish this, remove small amounts of suspension with a hypodermic needle at the exact height of each particle size that start to exhibit a rise in cmp (with the suspension in a Pyrex beaker). Use a geared vernier scale, or a break strength tester, to smoothly adjust the height of the tip of the hypodermic needle in the suspension. Then, the suspensions at each affected particle size can be examined microscopically for flocculation under dark field illumination. The analysis should also be done to the minimum particle size of 0.1 μm to see if the flocculation of these smallest particles did not cause the increase in cmp at 2 μm and higher. The smallest particles will then show a simultaneous decrease in cmp, or completely disappear.

3. The density of flocks can be determined by means of the microscope and timing mechanism of a zeta-potential meter that is turned on its side.

5. TESTING THE EFFECT OF SWELL-CLAYS ON ACCURACY

To conclude this study, tests were conducted on Na- and Ca-montmorillonite to illustrate the magnitude of the effects of different deflocculant types on their swelling, and the error caused by the difference between the densities of the components of clay mixtures and the average density that is used to calculate the scan rate.

One of the causes for inaccuracy during particle size analysis of swell-clays, and clay mixtures containing them, is the modification of particle sizes of Ca- and Na- montmorillonite in the unavoidable presence of a deflocculant. In the presence of a deflocculant, the following need to be kept in mind:

- the solid concentration of a suspension that is deflocculated for particle size analysis must preferebly be below 1.23% by volume, to prevent it from gelling if Na-montmorillonite is present (Watts *et al.*, 2000).
- in the presence of a deflocculant, Na-montmorillonite should disperse into single unit-layers (section 1.5.8.2.2); in this way its particle size is reduced to a minimum
- Ca-montmorillonite does not swell at all in the presence of a deflocculant; it collapses completely to a minimum particle size due to the loss of all of its interstitial cations (section 1.5.8.2.2).
- swelling is increase by the high pH (9.5) that is used to improve deflocculation (section 1.5.8.2.3).

Therefore, before starting to experiment with clay mixtures, the first logical step was to experimentally determine the lowest clay concentration the Sedigraph 5000D could allow to avoid the expected gelling of montmorillonite (section 4.2.2.2). The next step was to determine whether only desalination and increasing the pH would provide equally sufficient deflocculation of clay minerals as when a chemical deflocculant is used (reported in section 4.1.2.3). If successful, the above effect of deflocculants on the density of swell-clays can be avoided.

Apart from changing the particle size, clay-swelling can also cause accuracy problems related to the accompanying change in density. As *single clays*, Na- and Ca- montmorillonite can be analysed accurately, since their densities in the presence of a deflocculant is known.

Ca-montmorillonite collapses completely and the Na-form swells to a d_{001} spacing of about 563 Å in the presence of a dispersant. Hence, the Ca-form will have a density of 3.00 g/cm^3 during particle size analysis with Dispex, while for the Na-form the density will be about 1.034 g/cm^3 (section 1.5.8.4.2). However, it is not known whether the other deflocculants will have the same effect, and will therefore cause the same density during particle size analysis. Therefore, Na- and Ca-montmorillonite were also analysed when deflocculated with Calgon and Floccotan, and the results compared with that of Dispex.

When swell-clays, furthermore, are present in *clay mixtures*, they should adversely affect the analysis results. When analysing a mixture with a sedimentary method, the average density must be used to calculate the particle size (section). However, the true densities of the swell-clay components of mixtures will differ much more from the average density than those of their non-swelling counterparts. Therefore, the larger the swell-clay component, the more inaccurate the analyses results will be. The magnitude of the errors induced by swell-clays was therefore experimentally determined, by investigating self-made clay mixtures. These mixtures were made up at chosen ratios of kaolinite, montmorillonite, and illite in both their Ca- and Na-forms.

5.1 THE EFFECT OF DIFFERENT DEFLOCCULANTS ON THE PARTICLE SIZE OF Ca-MONTMORILLONITE

The attempt to circumvent the inevitable modification of Na- and Ca-montmorillonite particle size brought about by Dispex, by desalinating a clay suspension and raising pH, was clearly unsuccessful (section 4.1.2.3). A last attempt was to explore the possibility that other dispersant types might be used in place of Dispex for both the Na- and Ca-forms of montmorillonite.

To investigate this, three Blaauboschpoort montmorillonite samples were first converted to the Ca-and Na-forms, and then analysed for particle size in the presence of Dispex, Calgon, and Floccotan. A comparison of the cmp values of Dispex samples of Ca- and Na-montmorillonite with that of Calgon and Floccotan samples, would show whether the latter would cause less modification of particle size.

Materials and Methods:

Before converting the samples into the Ca-form with $CaCl_2$, they had to be centrifugally washed. This was to remove from the montmorillonite any excess Na_2CO_3, which was added by the supplier to convert the clay to its Na-form. Otherwise, if $CaCl_2$ was added to exchange the inter-layer Na^+ with Ca^{2+}, any excess $CO_3^=$ would have combined with Ca^{2+}, to form insoluble $CaCO_3$ that could have acted as a cementing material.

The montmorillonite sample was supplied as agglomerates of rice-size, and smaller. Therefore, the sample was first ground by mortar and pestle, followed by dry sieving. An initial trial disclosed that overnight soaking softened the montmorillonite aggregates. Despite this, the larger ones were not broken up completely by ultrasonic treatment. The reason probably was that only smaller agglomerates, with sizes in the order of cavitation bubbles, are broken in half during ultrasonic treatment. Larger agglomerates are rather *eroded* away slowly, by stripping smaller particles from it (Kusters *et al.*, 1994). The process is so slow that the larger agglomerates are not eroded to breakable size before the 3 min. ultrasonic time is up. Therefore, after grinding, agglomerates larger than 213 μm were first removed by dry sieving. Thereafter ultrasonic treatment could be completed successfully within 3 min.

The small fraction was shaken in a closed plastic container to attain homogeneous samples. Shaking was performed for 1 min., while tumbling and rotating the container in an irregular fashion. This was to prevent the separation of smaller and larger agglomerates by gravity: the smaller particles below, and the larger ones above, as would have happen if the container remained in an upright orientation during shaking. Clear evidence of the latter can be seen in samples being sieved on a sieve-shaker.

The montmorillonite sample had a yellow-brown colour, indicating the presence of iron oxide. The samples were therefore soaked overnight to soften its aggregates, and then ultrasonicated for 15 min. each to disperse them completely. This was to ensure that all clay particles were available for cation exchange, and to additionally secure accurate particle size analysis results of individual particles. After sieving and homogenisation, 100 ml of distilled water was added to three 10 g montmorillonite samples. After overnight soaking, the samples were shaken, and then centrifuged at 6000 rpm for 15 min. This was found to be enough to deposit all particles, but not too severe as to cause such dense sediments that their subsequent re-suspension by shaking was impeded.

The above centrifugal washing was repeated with 100 ml of a 50:50 methanol/distilled water mixture, followed by two methanol centrifugal washings. Thereafter the samples were

re-suspended with 100 ml of a 1N $CaCl_2$ solution, and centrifuged until the supernatant was clear. This was repeated for another three times to complete the Ca^{2+} exchange-saturation (Whittig and Allardice, 1986).

After cation exchange, all excess $CaCl_2$ was removed by centrifugal washing with distilled water at pH 4.5 to facilitate flocculation. Just prior to centrifugation, the pH of the suspensions was first adjusted with a few drops of HCl. Preceding that, to further aid flocculation, all samples were heated to 80 °C in a water bath. Centrifugal washing was repeated, until the supernatant of the last washing tested negative for Cl^- with 0.01M $AgNO_3$.

The three deposited clay samples were then re-suspended with 50 ml of distilled water, plus 25 ml of 6g/l Dispex, Calgon, or Floccotan, respectively. This quantity of deflocculants provided 1.5% deflocculant concentrations, and at the same time facilitated the re-suspending of sediments.

All samples were transferred to 100 ml Pyrex beakers of known mass. While weighing them on a 3 decimal scale, the samples were diluted to a solid concentration above what is required for Sedigraph analysis (9.52% $^{W}/_{W}$). This was achieved by adding an appropriate mass of distilled water to all suspensions to reach a 11.11 % $^{W}/_{W}$ solid concentration. The final mass of the Pyrex beakers plus clay suspension to obtain this, was calculated as follows:

Filled mass = 10g clay + 55g dist. water + 25 g deflocculant + empty mass of Pyrex beaker

Just before particle size analyses, an additional 5 min. ultrasonic treatment was applied to each sample. Thereafter the samples were wet-sieved through a 53 µm grid, facilitated by a rubber policeman. Wet sieving was regarded as necessary, since during the initial pulverisation in mortar and pestle the grinding sound of quartz particles was heard and felt under the pestle.

Finally, particle size analyses were conducted. To satisfy the Sedigraph requirements for accurate analysis, each sample was further diluted with distilled water during 100% adjustments until the required X-ray intensity was reached at a scan rate of 500. During each subsequent analysis, the scan rates calculated for Ca- montmorillonite were used (Table 5.1.3).

The size distributions of the Ca-montmorillonite suspensions with three different deflocculants are presented in Table 5.1.1. To allow comparison between the effect of Dispex on Ca-montmorillonite with those of the other two deflocculants, their cmp values at selected particle sizes were subtracted from those with Dispex.

Table 5.1.1. The effect of three different deflocculant types on the particle size distribution of Ca-montmorillonite

EQ. SPH. DIAMETER (μm)	CUMULATIVE MASS PERCENTAGE				
	DISPEX 1.5% SAMPLE	CALGON 1.5% SAMPLE		FLOCCOTAN 1.5% SAMPLE	
			Difference with Dispex 1.5% sample		Difference with Dispex 1.5% sample
1	63.5	60.0	-3.5	59.6	-3.9
2	72.6	69.0	-3.6	68.3	-4.3
3	80.4	75.5	-4.9	75.2	-5.2
4	85.7	82.0	-3.7	80.8	-4.9
5	90.2	87.0	-3.2	85.2	-5.0
6	93.8	90.8	-3.0	89.0	-4.8
8	97.8	95.6	-2.2	94.4	-3.4
10	99.8	98.0	-1.8	97.0	-2.8
20	100.0	100.0	0.0	99.8	-0.2
30	100.0	100.0	0.0	100.0	0.0

Results and Discussion:

Dispex reduced the cmp of Ca-montmorillonite most of all deflocculants, closely followed by Calgon and then Floccotan. The largest cmp difference with that of Dispex was when Ca-montmorillonite was dispersed with Floccotan. It gave a −5.2% cmp difference at 3 μm. The larger cmp values of Dispex imply that it induced smaller particle sizes than the other two deflocculants at same cmp values. This was especially the case in the middle and smaller esds.

Conclusions:

1. Since both Calgon and Floccotan samples had particle sizes of the same order as the Dispex sample, it can be concluded that all of the deflocculants substantially reduce the particle size of Ca-montmorillonite. However, the decrease of the Ca-montmorillonite particle size by Dispex was somewhat larger than was the case with Calgon and Floccotan. Using deflocculants other than Dispex during particle size analysis therefore cannot avert the modification of the particle size of Ca-montmorillonite.
2. Due to the diverse swelling of Ca-montmorillonite with different deflocculants, there is a significant variation in cmp between them (differences between 0.2% cmp, to as high as 5.2% cmp are evident). Therefore, it is important that only one type of dispersant is used when comparisons are made between the particle size analyses of different samples containing any swell-clays.

3. Since it is known from the XRD analysis of Morvan *et al.* (1994) that Ca-montmorillonite exhibits no swelling with Dispex, it was decided to use Dispex to disperse Ca-montmorillonite samples, and any clay mixtures containing it (section 5.1). This will allow the known density of 3.00 g/cm^3 of completely collapsed montmorillonite to be used to calculate the Sedigraph cell scan rate for Ca-montmorillonite.

Recommendations for further study:

1. Analyse Ca-montmorillonite with XRD when dispersed with several different concentrations of Calgon, Floccotan and TSP to affirm to what extent these deflocculants will collapse Ca-montmorillonite. As a control, duplicate the XRD analyses for all three deflocculants combined with the other more common K^+-, Mg^{2+}-, and Al^{3+}-versions of montmorillonite. With the help of the d-spacings of every sample, calculate their densities from their Monte Carlo data. Also conduct particle size analysis on the K^+-, Mg^{2+}-, and Al^{3+}-versions of montmorillonite when dispersed with all three deflocculants, to see to what degree their control of swelling causes differences in particle size.
2. Verify that the density of Ca-montmorillonites is in fact at 3.00 g/cm^3 by using pycnometric density determinations of four different Ca-montmorillonite samples dispersed in Dispex, Calgon, Floccotan, and TSP, respectively.
3. A Dispex concentration of 1.5% was assumed sufficient to assure accurate particle size analysis with Ca-montmorillonite. It was reasoned that since this is double the amount of Dispex needed for the finest kaolinite (Amazone), it should therefore be more than enough to disperse montmorillonite. A 1.5% Dispex concentration was furthermore viewed as not high enough to cause flocculation due to over-dispersion. These assumptions, though, need to be validated for montmorillonite experimentally.
4. The tests for optimum dispersant concentration (similar to those for kaolinite in section 4.1.2.1) should be extended to include illite, and all the other smectites (beidellite, nontronite, saponite, hectorite, sauconite), as well as for the less common clay minerals like gibbsite and the attapulgite-palygorskite-sepiolite series of clay minerals.
5. Other common soil minerals (*e.g.* quartz, vermiculite and chlorite) may sometimes be found within the particle size range of clays, and should therefore be included in tests of clay mixtures. Additional tests for optimum dispersant concentration should therefore be conducted for each of these soil minerals, to assure that the dispersant concentration used with clay mixtures is correct for all potential components.

5.2 THE MAGNITUDE OF INACCURACY WHEN CLAY MIXTURES CONTAIN SWELL-CLAYS

Swell-clays will not only give inaccurate sedimentary particle size analysis results on their own, but when they are present in clay mixtures, results will be adversely affected also. Especially the differences between the true densities of separate swell-clay components and the average density (needed to calculate scan rate) will have the largest contribution to the inevitable cmp errors. Hence, the size of the effect of the presence of swell-clays on the accuracy of clay mixtures had to be determined also.

To investigate the effects of the differences between the average density of clay mixtures and those of their swell-clay components, a series of mixtures were made up. They consisted of different ratios of three different clay types: kaolinite, illite, and montmorillonite. Initially, all single clay types, and their mixtures, were centrifugally washed to remove all excess soluble salts, and then they were exchanged with Ca^{2+}.

The first step was to obtain the particle size distributions of each of the three single clay types. Next, several clay mixtures were made up at known mass fractions of each clay type. Then, from the experimental particle size distributions of each individual clay type, a *theoretical* particle size distribution for each mixture was calculated according to the mass fraction of each clay type present.

Finally, a particle size analysis was carried out on each clay mixture. The cmp values of the theoretical and the experimental particle size distributions for each clay mixture were subtracted from each other. This gave the error caused by the differences between the real densities of the individual components, and the average density used to calculate the scan rate of the mixture.

Materials and Methods:

Both the illite and montmorillonite samples were pulverised beforehand in a mortar and pestle. Then they were dry-sieved at 213 μm to facilitate accurate weighing. To attain as homogeneous as possible dry samples, the sieved samples were shaken in a closed plastic container, while rotating and tumbling it in an irregular fashion for 1 min.

Next, four mixtures were made up at different ratios of Serina filler 1 kaolinite, illite, and montmorillonite to a total of 10 g each. The chosen clay mass-fraction used for each clay type is listed in Table 5.2.1. The dry clay mass of each clay component to afford each chosen clay

ratio was also calculated.

Table 5.2.1. Clay mass fraction, and needed clay mass for 4 different clay mixtures

SAMPLE No.	CLAY MASS FRACTION OF EACH MIXTURE COMPONENT			DRY CLAY MASS (g) OF EACH MIXTURE COMPONENT		
	Ca-Montm.	Ca-Illite	Ca-Kaolinite	Ca-Montm.	Ca-Illite	Ca-Kaolinite
1	0	**1**	0	0	**10**	0
2	0	0	**1**	0	0	**9**
3	**1**	0	0	**10**	0	0
4	0.75	0.20	0.05	7.50	2.00	0.50
5	0.05	0.75	0.20	0.50	7.50	2.00
6	0.33	0.33	0.33	3.33	3.33	3.33
7	0.20	0.05	0.75	2.00	0.5	8

To ensure that the correct mass of the montmorillonite component was added too each clay mixture, it was first dried overnight in an oven at 100 °C to remove surface adsorbed water. Afterwards it was cooled in a desiccator in dry air, over silicone. Thereafter the different clay mixtures were made up on a scale in plastic sample bottles according to the clay component proportions given in Table 5.1.1. Weighing was conducted accurate to the third decimal. It was completed quickly, to prevent a rise in montmorillonite mass due to re-adsorption of ambient moisture.

Additionally 10g samples, each consisting only of the single minerals of Serina filler 1 kaolinite, illite, and montmorillonite, were also weighed off. Thereafter all samples were centrifugally washed with distilled water to remove any soluble salts (especially any excess Na_2CO_3 in the montmorillonite sample). To flocculate the suspension during centrifugal washing, the pH was adjusted to 4.5 with 0.02 M HCl, followed by heating in a water bath to 80 °C just before centrifugation.

To effect Ca^{2+} exchange, the centrifuged samples were re-suspended with 1N $CaCl_2$ solution, ultrasonicated for 3 min., and left overnight for the exchange equilibrium to be reached. The next morning it was centrifuged until the supernatant was clear. Afterwards all excess $CaCl_2$ was removed by centrifugal washing with distilled water, followed by a 50:50 distilled water/methanol mixture, and lastly twice with methanol only. When adding a few drops of 0.01M $AgNO_3$ to the supernatant after the last washing, it tested negative for Cl^-.

After the last washing, the all clay samples were re-suspended from the bottoms of the centrifuge tubes with 50 ml of distilled water plus 25 ml of Dispex (6g/l), to obtain a 1.5% deflocculant concentration. Then they were transferred to 100 ml Pyrex beakers of known mass, and diluted to a solid concentration 11.11 % by weight with the identical methods as used in section 5.1. Thereafter all the samples containing illite or Ca-montmorillonite were wet-sieved through a 53 μm grid, facilitated by a rubber policeman (the Serina sample was known to be 100% below 30 μm).

Before the samples could be analysed, though, the average densities of each of the clay mixtures had to be calculated by using the volume-fraction of each clay type in the mixture. First, the densities for kaolinite (2.63 g/cm^3), illite (2.75 g/cm^3), and Ca-montmorillonite (3.00 g/cm^3), along with the chosen mass fractions in Table 5.1.1, were used to calculate the volume fractions of each clay type of each mixture (Table 5.2.2). Then the volume fractions were inserted in the formula of Chandrasekhar (1994) to calculate the average density of each mixture (section 2.11).

Table 5.2.2. Calculating the density of the different clay mixtures containing Ca-montmorillonite when dispersed with Dispex

SAMPLE No.	CLAY VOLUME FRACTION OF EACH MIXTURE COMPONENT			DENSITY OF CLAY MIXTURE
	Ca-Montm.	Ca-Illite	Ca-Kaolinite	(g/cm^3)
1	0	**1**	0	2.75
2	0	0	**1**	2.63
3	**1**	0	0	3.00
4	0.80	0.16	0.04	2.94
5	0.06	0.73	0.20	2.74
6	0.39	0.30	0.31	2.81
7	0.24	0.05	0.71	2.72

Lastly, using the average densities, the cell scan rates for each clay mixture were calculated (Table 5.1.3). During this calculation, a density of 2.75 g/cm^3 was used for illite (Deer *et al.*, 1966). For Ca-montmorillonite the density of 3.00 g/cm^3 at the fully collapsed state was used – as expected when in the presence of a deflocculant (section 1.5.8.2.2). The whet-sieving was conducted after a standard 3 min. ultrasonic treatment. Since all the samples containing illite or Ca-montmorillonite were wet-sieved at 53 μm, the D_{max} for scan rate

calculations was chosen as 55 µm during each subsequent analysis.

Just prior to the analysis of every single clay type and each clay mixture, the pH was adjusted to 9.5 with Na_2CO_3, to ensure optimal chemical dispersion. The experimental particle size distributions of the Ca-forms of the three single clays, along with that of their mixtures and their calculated accurate particle size distributions, are presented in Table 5.2.4. The errors in cmp at each esd were calculated by subtracting the experimental cmp values from the calculated ones (Table 5.1.4). Ultimately the average error over all particle sizes for each was computed.

Results and Discussion:

The pattern of the errors in Table 5.2.4 discloses that most cmp errors are positive. This indicates that for the majority of the analysis results the cmp values of clay mixtures were too high. Hence, due to the need to use an average density the particle sizes were inevitably under-estimated.

The mixture of equal ratio for all three clays gave the largest errors of up to 4.7% cmp with an average error of 2.3% cmp (sample 6). The next largest inaccuracy was for sample 7 containing 75% Ca-kaolinite with a maximum error of 3% (average error 1.5%), and for sample 4 containing 75% Ca-montmorillonite, also with a maximum error of 3% (average 1.1%). The sample giving the smallest errors was sample 5, containing 75% Ca-illite, which has a maximum error of 1.5% cmp (average error 0.3%).

Different particle sizes had unlike cmp errors – with the bigger errors for some mixtures in the middle particle sizes, and for others in the small particle sizes.

Since many factors will play a role to determine the size of the error, it is difficult to decide why the above error pattern emerged. Amongst the reasons must be the magnitude of the difference between the density of the clay component and the average density, the relative amount of each clay type, and the difference in cmp with the other components at every particle size.

Table 5.2.3. The calculated rate for every clay mixture containing swell-clays, when dispersed with Dispex

MEASURED TEMP. (°C)	CALCULATED DENSITY (g/cm^3)	CALCULATED VISCOSITY (C.Poise)	CALCULATED RATE (D-Max. = 55 µm) Sample 1 (Ca-Illite)	Sample 3 (Ca-Mont.)	Sample 4	Sample 5 (*Mixtures*)	Sample 6	Sample 7
30.1	0.9956204	0.7927	681	778	754	677	704	584
30.2	0.9955901	0.7910	682	779	756	678	705	585
30.3	0.9955596	0.7894	684	781	758	680	707	586
30.4	0.9955292	0.7877	685	783	759	681	708	587
30.5	0.9954986	0.7860	686	784	761	683	710	589
30.6	0.9954679	0.7844	688	786	762	684	711	590
30.7	0.9954371	0.7827	689	788	764	685	713	591
30.8	0.9954063	0.7810	691	789	766	687	714	592
30.9	0.9953754	0.7794	692	791	767	688	716	594
31.0	0.9953444	0.7778	694	793	769	690	718	595
31.1	0.9953133	0.7761	695	794	771	691	719	596
31.2	0.9952821	0.7745	697	796	772	693	721	597
31.3	0.9952508	0.7729	698	798	774	694	722	599
31.4	0.9952195	0.7713	700	799	775	696	724	600
31.5	0.9951880	0.7697	701	801	777	697	725	601
31.6	0.9951565	0.7681	703	803	779	699	727	603
31.7	0.9951249	0.7665	704	804	780	700	728	604
31.8	0.9950932	0.7649	706	806	782	702	730	605
31.9	0.9950614	0.7633	707	808	784	703	731	606
32.0	0.9950296	0.7617	709	810	785	705	733	608
32.1	0.9949976	0.7601	710	811	787	706	734	609
32.2	0.9949656	0.7585	712	813	789	707	736	610
32.3	0.9949335	0.7570	713	815	790	709	737	611
32.4	0.9949013	0.7554	715	816	792	710	739	613
32.5	0.9948690	0.7538	716	818	794	712	740	614
32.6	0.9948366	0.7523	718	820	795	713	742	615
32.7	0.9948042	0.7507	719	821	797	715	744	617
32.8	0.9947717	0.7492	720	823	798	716	745	618
32.9	0.9947390	0.7477	722	825	800	718	747	619
33.0	0.9947063	0.7461	723	827	802	719	748	620
33.1	0.9946736	0.7446	725	828	803	721	750	622
33.2	0.9946407	0.7431	726	830	805	722	751	623
33.3	0.9946078	0.7416	728	832	807	724	753	624
33.4	0.9945747	0.7401	729	833	808	725	754	626
33.5	0.9945416	0.7386	731	835	810	727	756	627
33.6	0.9945084	0.7370	732	837	812	728	758	628
33.7	0.9944752	0.7356	734	839	813	730	759	629
33.8	0.9944418	0.7341	735	840	815	731	761	631
33.9	0.9944084	0.7326	737	842	817	733	762	632
34.0	0.9943748	0.7311	739	844	818	734	764	633
34.1	0.9943412	0.7296	740	845	820	736	765	635
34.2	0.9943076	0.7281	742	847	822	737	767	636
34.3	0.9942738	0.7267	743	849	823	739	768	637
34.4	0.9942400	0.7252	745	851	825	740	770	639
34.5	0.9942060	0.7238	746	852	827	742	772	640
34.6	0.9941720	0.7223	748	854	828	743	773	641
34.7	0.9941379	0.7209	749	856	830	745	775	642
34.8	0.9941038	0.7194	751	857	832	746	776	644
34.9	0.9940695	0.7180	752	859	834	748	778	645
35.0	0.9940352	0.7165	754	861	835	749	779	646

Table 5.2.3 Continued

MEASURED TEMP. (°C)	CALCULATED DENSITY (g/cm^3)	CALCULATED VISCOSITY (C.Poise)	CALCULATED RATE (D-Max. = 55 µm) Sample 1 (Ca-Illite)	Sample 3 (Ca-Mont.)	Sample 4 (*Mixtures*)	Sample 5 (*Mixtures*)	Sample 6 (*Mixtures*)	Sample 7 (*Mixtures*)
35.1	0.9940008	0.7151	755	863	837	751	781	648
35.2	0.9939663	0.7137	757	864	839	752	783	649
35.3	0.9939317	0.7123	758	866	840	754	784	650
35.4	0.9938971	0.7108	760	868	842	755	786	652
35.5	0.9938624	0.7094	761	870	844	757	787	653
35.6	0.9938276	0.7080	763	871	845	758	789	654
35.7	0.9937927	0.7066	764	873	847	760	790	656
35.8	0.9937577	0.7052	766	875	849	761	792	657
35.9	0.9937227	0.7038	767	877	850	763	794	658
36.0	0.9936876	0.7025	769	878	852	765	795	659
36.1	0.9936524	0.7011	770	880	854	766	797	661
36.2	0.9936171	0.6997	772	882	855	768	798	662
36.3	0.9935817	0.6983	774	884	857	769	800	663
36.4	0.9935463	0.6969	775	885	859	771	802	665
36.5	0.9935108	0.6956	777	887	861	772	803	666
36.6	0.9934752	0.6942	778	889	862	774	805	667
36.7	0.9934395	0.6929	780	891	864	775	806	669
36.8	0.9934037	0.6915	781	892	866	777	808	670
36.9	0.9933679	0.6902	783	894	867	778	809	671
37.0	0.9933320	0.6888	784	896	869	780	811	673
37.1	0.9932960	0.6875	786	898	871	781	813	674
37.2	0.9932599	0.6861	787	899	873	783	814	675
37.3	0.9932238	0.6848	789	901	874	784	816	677
37.4	0.9931876	0.6835	790	903	876	786	817	678
37.5	0.9931513	0.6821	792	905	878	788	819	679
37.6	0.9931149	0.6808	794	907	879	789	821	681
37.7	0.9930785	0.6795	795	908	881	791	822	682
37.8	0.9930419	0.6782	797	910	883	792	824	683
37.9	0.9930053	0.6769	798	912	885	794	826	685
38.0	0.9929687	0.6756	800	914	886	795	827	686
38.1	0.9929319	0.6743	801	915	888	797	829	687
38.2	0.9928951	0.6730	803	917	890	798	830	689
38.3	0.9928582	0.6717	804	919	891	800	832	690
38.4	0.9928212	0.6704	806	921	893	801	834	691
38.5	0.9927841	0.6691	808	923	895	803	835	693
38.6	0.9927470	0.6679	809	924	897	805	837	694
38.7	0.9927098	0.6666	811	926	898	806	838	695
38.8	0.9926725	0.6653	812	928	900	808	840	697
38.9	0.9926351	0.6641	814	930	902	809	842	698
39.0	0.9925976	0.6628	815	931	904	811	843	699
39.1	0.9925601	0.6615	817	933	905	812	845	701
39.2	0.9925225	0.6603	819	935	907	814	847	702
39.3	0.9924849	0.6590	820	937	909	815	848	703
39.4	0.9924471	0.6578	822	939	911	817	850	705
39.5	0.9924093	0.6565	823	940	912	819	851	706
39.6	0.9923714	0.6553	825	942	914	820	853	708
39.7	0.9923334	0.6541	826	944	916	822	855	709
39.8	0.9922954	0.6528	828	946	918	823	856	710
39.9	0.9922573	0.6516	830	948	919	825	858	712
40.0	0.9922191	0.6504	831	949	921	826	860	713

Table 5.2.4. The actual and calculated particle size distributions of mixtures of Ca-illite, Ca-kaolinite, and Ca-montmorillonite, and the errors in cmp for the different mixtures thereof

EQ. SPH. DIA. (μm)	CUMULATIVE MASS PERCENTAGE														
	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**			**Sample 5**			**Sample 6**			**Sample 7**		
	(Ca-Illite)	(Ca-Kaol.)	(Ca-Mont.)	Experimental	Calculated	Error	Experimental	Calculated	Error	Experimental	Calculated	Error	Experimental	Calculated	Error
55	100.0	100.0	100.0	100.0	100.0	0.0	100.0	100.0	0.0	100.0	100.0	0.0	100.0	100.0	0.0
40	100.0	100.0	100.0	100.0	100.0	0.0	100.0	100.0	0.0	100.0	100.0	0.0	100.0	100.0	0.0
30	97.5	100.0	99.9	99.8	99.4	0.4	98.7	98.1	0.6	99.4	99.1	0.3	100.0	99.9	0.1
20	84.7	100.0	98.3	97.3	95.7	1.6	89.9	88.4	**1.5**	95.7	94.3	1.4	98.9	98.9	0.0
10	61.8	94.4	88.5	84.5	83.5	1.0	70.3	69.7	0.6	83.8	81.6	2.2	93.8	91.6	2.2
8	56.4	91.0	83.6	80.1	78.5	1.6	65.0	64.7	0.3	79.2	77.0	2.2	90.1	87.8	2.3
6	50.6	85.2	77.3	73.8	72.4	1.4	59.0	58.9	0.1	73.4	71.0	2.4	84.9	81.9	**3.0**
5	46.5	81.2	72.6	69.0	67.8	1.2	54.8	54.7	0.1	69.2	66.8	2.4	80.0	77.7	2.3
4	42.8	75.7	68.6	64.9	63.8	1.1	50.3	50.7	-0.4	65.1	62.4	2.7	74.6	72.6	2.0
3	38.3	68.4	64.2	60.0	59.2	0.8	45.2	45.6	-0.4	60.0	57.0	3.0	66.3	66.1	0.2
2	33.5	57.6	55.7	54.4	51.4	**3.0**	40.0	39.4	0.6	53.6	48.9	**4.7**	57.9	56.0	1.9
1	26.4	43.1	51.2	46.2	45.8	0.4	31.7	31.0	0.7	44.3	40.2	4.1	46.8	43.9	2.9
Average Error:						1.1			0.3			2.3			1.5
pH:	9.22	7.54	8.41	8.26			?			8.37			7.52		
Adjusted pH:	9.54	9.52	9.53	9.52			9.51			9.49			9.50		

Another probable cause for the differences in the size of the errors is the X-ray absorbency of iron oxides present in diverse amounts in both the illite and montmorillonite samples (as characterised by their yellow-brown colour). Since iron will attenuate X-rays more than the aluminium in the clay particles themselves, the particle sizes of each iron oxide-rich component will be over-estimated in cmp (Coakley and Syvitski, 1991). Moreover, iron oxides can also be more concentrated in a specific particle size range (Watts *et al.*, 2000). Consequently, a clay sample that has this specific particle size range in abundance, would experience a larger cmp overestimation in that part of its particle size distribution curve.

Conclusions:

1) When analysing *clay mixtures* with the sedimentary methods, cmp values are appreciably over-estimated (between 1.5% and 4.7%). Accordingly, the particle sizes are under-estimated by significant amounts. This occurs despite the fact that the average density of a clay mixture is determined by taking into account the volume fraction of each of the components.

2) The amount of swell-clays in mixtures did not affect the magnitude of the error as much as was expected. The reason probably was that the presence of organic material and iron oxides on the clay surfaces restricted the collapse of sizeable amounts of particles.

   The possible restrictive effect of organic material and iron oxides actually now allows the deduction to be made that the difference between the densities of the individual components and that of the calculated average density is large enough to significantly affect the accuracy of sedimentary particle size analysis results of clay mixtures. Proof of this is that when all three components are at equal amounts (sample 6), then the error is largest. Here the density of illite (2.75 g/cm^3) was close to the average of the mixture (2.81 g/cm^3), but *two components* had large differences with the average *viz.* kaolinite (2.63 g/cm^3) and Ca-montmorillonite (3.00 g/cm^3 – see Table 5.1.2). If there is no restrictive effect, the error should be larger where Ca-montmorillonite was in excess.

Recommendations for further study:

1. Duplicate the above test with the same samples. But as a pre-treatment, use the relevant dissolution methods described in section 5.1.3. Thus will be removed all substances that can bring about too large particle sizes when aggregates are only partially broken up by ultrasonic treatment. It will also prevent the restriction of swelling or shrinkage during

cation exchange and water absorption/desorption.

2. Using chemical dissolution methods as standard procedure will simultaneously avert the use of severe ultrasonic treatment needed to break up hard aggregates – in fact, in many cases ultrasonic treatment is unsuccessful to effect complete de-aggregation, which makes prior dissolution a necessity (Arustamyants, 1991).

   Should the samples, furthermore, be kept wet after the centrifugal washing following dissolution, it is conceivable that mild ultrasonic treatment will be enough to break up any weaker agglomerates that had formed due to van der Waals attraction during deposition under centrifugal force. Agglomerates will also inevitably have formed due to the same reason when the clay was dried out, and milled to sugar-sized agglomerates before initial weighing. It is not sure whether dissolution will break up any of these agglomerates. The inferred need for additional ultrasonic treatment after dissolution should be verified also.

3. Conduct a literature search on the organic substances used to restrict the swelling of montmorillonite in drilling mud (Roodt, 1998). Investigate the possibility of using this to restrict the swelling of Na-montmorillonite in the presence of deflocculants.

4. Vermiculite is a plate-silicate that may form together with illite, montmorillonite, and kaolinite during the weathering of rock silicates (Eberl, 1984). Vermiculite is therefore commonly found in soils. Although not regarded as a clay mineral by some sources, it has a very similar structure and composition as clay minerals (notably chlorite). It also contains water molecules between its unit-layers, but its d_{001} spacing is less variable than that of the smectites (Deer *et al.*, 1966). Since vermiculite has a very small particle size, it is also contained in the clay fraction of sediments and soils. It is therefore advisable that it should be included in mixtures when investigating its accuracy with sedimentary methods. Also investigate whether chlorite can be present in the sub 55 μm soil fraction. If so, include it as a component in some of the mixtures.

5. Na-montmorillonite will be of a much smaller density than the average density of most mixtures containing it. It will therefore give much larger errors than its Ca-form. Montmorillonite – especially when in the Na-form – will also form mixed-layered minerals along with illite (possibly also with kaolinite), when a suspension containing them is agitated. Therefore, repeat the above experiment with mixtures containing Na-montmorillonite. It must be conducted, though, at a solid concentration below 1.13% by volume to prevent gelling.

6. SUMMARY AND CONCLUSIONS

In this last chapter the following will be presented:

- a short summary of the unique properties of clays setting them apart from other mineral particles during sedimentary particle size analysis
- the significance of each of these properties to accuracy and reproducibility
- an evaluation of the validity of using sedimentary particle size analysis results of swell-clays to characterise their natural environments
- based on all the above, a short summary of the correct approach to all gravitational sedimentary methods is given
- a standard method is proposed for all sedimentary methods for all types of clay minerals and clay mixtures
- the material-related parameters affecting all sedimentary methods, along with the magnitudes of their effects on accuracy and reproducibility, is provided in table-form.

6.1 IMPLICATIONS OF THE UNIQUE PROPERTIES OF CLAYS TO ACCURACY AND REPRODUCIBILITY OF SEDIMENTARY METHODS

Effect of the wide size distribution of clays

The upper size limit for accurate sedimentary particle size analysis

The sizes of the largest clay particles in nature coincide with the *upper* size limit of 49.6 μm for the Sedigraph at its operational temperature of 35 °C (section 1.5.1.1.1). The upper size limit for the other sedimentary methods is slightly below this value because they are conducted at lower room temperatures. Since the particle sizes of other soil minerals frequently exceed the upper size limit, all samples need to be divided at approximately 50 μm prior to sedimentary analysis either by means of wet sieving, or by sedimentary size fractionation (Gee and Bauder, 1986).

The lower size limit for accurate sedimentary particle size analysis

The smallest natural clay particles, though, present a problem when using any sedimentary method. Due to the dispersive effect of Brownian movement on such small particles, they fall below this size limit of the Sedigraph (0.56 μm) (section 1.5.1.1.2). With the other sedimentary methods, conducted at lower room temperatures, the lower size limit is at slightly larger particle sizes. Most montmorillonite particles fall below the lower limit for accurate sedimentary particle size analysis. This is especially the case with Na-, Li+, and H-montmorillonite. Hence, the larger the montmorillonite content in a clay sample, the less accurate will be its particle size distributions of the smaller size fractions.

The particle size beneath which particles do no settle when suspended in water

There is an even lower size limit of 0.21 μm below which clay particles, due to Brownian diffusion, will not settle at all (section 1.5.5.2.1). The abovementioned 0.56 μm minimum size limit for accurate analysis is very close to 0.21 μm. This implies that below 0.56 μm, accuracy should decrease rapidly. Hence, analyses should rather not be conducted to equivalent spherical diameters (esds) close to, or below 0.56 μm.

With much larger sedimentationary force fields, the centrifugal methods have virtually no Brownian dispersion, even at this small particle size (0.56 μm). Therefore the magnitude of Brownian dispersion on accuracy close to the lower size limit (0.56 μm) can be illustrated by comparing the cmp values of the Sedigraph and the Andreasen method with that of the centrifugal methods (section 1.5.1.2). This comparison clearly illustrates the inaccuracy for the Sedigraph around the lower size limit for sedimentary particle size analysis: at 0.6 μm the Sedigraph has a 25.2% difference with the Laboratory centrifuge (Table 1.5.1.2.1). With the Andreasen pipette, the difference with the Laboratory centrifuge is very similar at 24.4%. However, beneath 1 μm, the error is in the order of only 0.5% (Table 1.5.1.2.1) Hence, if accuracy at the lower end is important, then sedimentary particle size analysis should not be conducted to esds smaller than 1 μm.

The minimum particle size for single particles when suspended in water

The aim of particle size analysis is to obtain the sizes of single particles. However, particles smaller than 0.1 μm will always flocculate despite the presence of a deflocculant, (section 1.5.5.2.1). It is therefore concluded that many 'particles' detected at smaller esds will actually be that of flocks, consisting of single particles smaller than 0.1 μm. It is therefore obvious that any clay, or clay mixture, containing a large enough fraction of smaller than

0.1 µm particles can not be analysed accurately with any particle size analysis technique: along with single particles, it will contain many flocks consisting of much smaller particles. Most montmorillonite particles fall within this size range (section 1.5.8.1). Therefore, due both to Brownian dispersion and flocculation, any substantial amount of montmorillonite in a clay sample will always cause inaccurate results at the smaller particle size end of the size distribution.

The effect of solid concentration on particle interactions

Effect of low concentration hindered settling on accuracy

At low solid concentrations, the accuracy of all sedimentary methods can be compromised by cluster formation due to low concentration hindered settling. For clay suspensions below *0.41% by volume* this effect *increases* the settling velocity of some of its particles due to cluster formation (section 1.5.2). At the larger esds this should cause higher cmp values than should be, whereas lower cmp values will be registered at the particle size fraction that should have contained the single particle components of clusters. Hence, to prevent *low* concentration hindered settling from affecting accuracy, solid concentrations of clay suspensions must be kept at, or above 0.41%. Since the Andreasen method is conducted at between 0.38% and 0.5% solid concentration, it should not be noticeably affected by low concentration hindered settling.

Effect of high concentration hindered settling on accuracy of the Sedigraph

Due to its low density, clay minerals have low X-ray absorbencies. To ensure accuracy with X-ray sedimentometers such as the Sedigraph, this creates the need for high solid concentrations (> 3.00% by volume). At solid concentrations higher than 1 %, however, so called *high concentration hindered settling* now comes into effect. In contrast to low concentration hindered settling, this effect increasingly *retards* the settling velocity of particles with increase in solid concentration (section 1.5.2.1.2). Hence, to avert both low and high concentration hindered settling, the solids concentration should be kept at between 0.4% and 1.0% by volume. Relatively accurate measurements, though, can still be conducted up to a volume concentration of 3%.

Since the Sedigraph 5000D handbook stipulates parameters causing solid concentrations of around 3.85% for clay suspensions, noticeable *inaccuracy* will already be caused for it due to this effect (sections 4.2.2.2 and 4.2.2.3). In section 4.2.2.2 the cmp difference was compared

between two Sedigraph solid concentrations (3.85% and 1.91%). There was no effect of high concentration hindered settling on accuracy at the larger particle sizes (0% cmp error at 20 μm – Table 4.2.2.2.1). But as particle sizes become smaller, the cmp error increased to >3.4% at 2 μm. A slight decline in the repeatability towards smaller particle sizes also was observed (section 4.2.2.3.1). Both these observations affirm that hindered settling increases with the Sedigraph as particles become smaller.

Inaccuracy caused by particle collisions

Due to particle collisions between faster moving larger particles and smaller, slower ones, the latter should rotate more than the larger ones. Due to their increased rotation, small particles will settle slower than should be, and should therefore register lower cmp values than should be (section 1.5.3). With larger particles, on the other hand, this effect should be much less. Rotational retardation of settling velocity should increase at larger solid concentrations since the particles are closer together, which increases the chances of collisions. During Sedigraph analyses at 3.85% solids, rotation due to particle collisions will therefore add to the inaccuracy caused by high concentration hindered settling.

Additionally, as particle collisions increase with the increase in solid concentration, smaller particles will increasingly be accelerated. Conversely, the larger faster moving particles, colliding with smaller slower moving ones, will be retarded somewhat. This will have the opposite effect as the rotation caused by the same collisions: collision acceleration will cause higher cmp values for smaller particles, while the larger particles will register lower cmp values. The balance between the effect of rotation retardation and collision acceleration of smaller particles, and the retardation of larger ones during collisions, will cause inaccurate particle size distributions for clay particles of which the magnitude is unknown.

Solids concentration and clay suspension stability

Lastly, when trying to disperse kaolinite in water by only desalination and increasing the pH (no chemical deflocculant), solid concentration is a large factor in its *stability*. At volume concentrations of above 1.91%, kaolinite suspensions are completely unstable under such conditions (section 4.1.2.3.1). The cause for the greater rate of flocculation with increased sold concentration is the larger chance of particle collisions due to Brownian vibrations. Due to this effect, when only dispersed by desalination and high pH, flocculation prevents the particle size analyses of clay suspensions at the typical solid concentration of the Sedigraph (3% to 4% by volume) (section 4.1.2.3.1).

Comparison between the Sedigraph and the Andreasen method

When Sedigraph analyses are conducted at the prescribed solid concentration of 3.85% by volume, it gives notably less accurate results than the Andreasen pipette method due to hindered settling and particle collisions. However, when it is conducted at the same low solid concentration of the Andreasen method (± 0.4% to 0.5%), their results compare very well (section 1.5.2.1.3). However, at these solid concentrations the Sedigraph gives more accurate results (section 1.5.2.1.3), and is up to 48X faster than the Andreasen method (section 1.4.2). It is therefore recommended that the Sedigraph should replace the Andreasen pipette as standard method for sedimentary particle size analysis of clays.

Solid concentration and repeatability

Repeatability of the Sedigraph is not seriously affected by high concentration hindered settling. At the minimum allowable solid concentration for the Sedigraph 5000D (3.85% by volume), its repeatability was slightly better than at 1.91% by volume (section 4.2.2.3). The Sedigraph repeatability at 3.85% solids is illustrated by the experimentally determined stdev of 0.22% cmp at 2 µm, and the maximum error fluctuation for all particle sizes of ± 0.55% (section 4.2.2.3.1). The latter significantly improves on the error fluctuation of the Sedigraph Instructions Manual (± 1%).

The excellent Sedigraph repeatability values firstly imply that the measures taken during this study to keep the apparatus-related parameters of the Sedigraph 5000D in check were successful (section 3). The second implication is that variations in the results when a single parameter was changed during this study were caused only by the change of that single parameter, and not by any discrepancies inherent to the material, the instrument, or the methodology.

The chemical deflocculant and repeatability

Whereas Dispex gave slightly better accuracy, the deflocculant that gave the best repeatability was Calgon, followed a bit further back in close order by Floccotan, TSP, and Dispex (section 4.2.3.2).

Clay particle shape and its significance to accuracy of the sedimentary methods

When measuring the particle size of clays with any sedimentary method, it must be kept in mind that the esd is the diameter of a sphere, whereas clay particles in reality are platelets or cylinders (Fig. 6.1.1). Their shape and dimensions therefore vastly differ from that of the

spherical shape (equivalent spherical diameter) determined by a sedimentary method. In reality, the true basal diameter of a clay platelet can be between 240% and 800% larger than its equivalent spherical diameter (esd), whereas its thickness can be as small as between 5% and 24% of the size of its experimentally determined esd (section 1.5.4). For halloysite, its cylinder length can be as much as 400% longer than the diameter (esd) obtained through a sedimentary method.

Hence, when determined by a sedimentary method, the diameters of clay particles do not even closely resemble their actual dimensions.

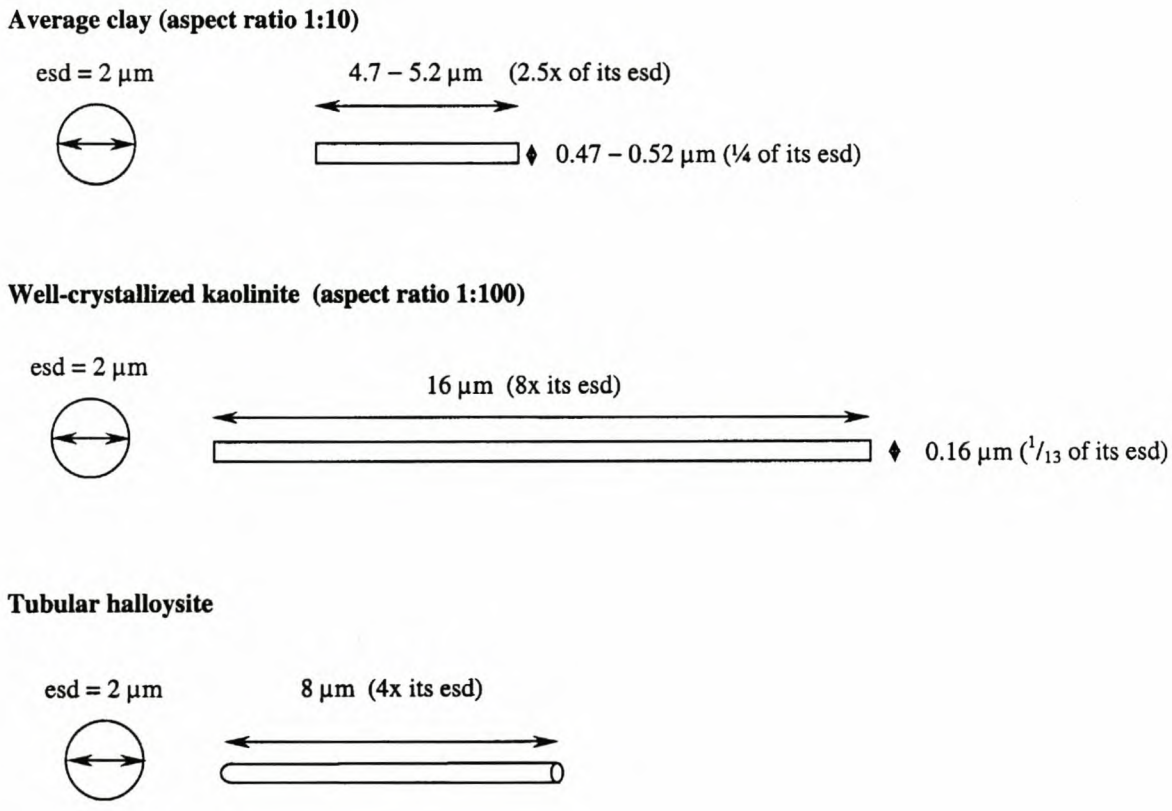


Fig. 6.1.1. The true clay particle dimensions vs. its experimentally determined esd (drawn to scale).

Increased tendency to flocculation due to clay particle shape and the unique dual nature of its surface charge

In order to safeguard its accuracy during any particle size analysis great care must be taken when dispersing clay suspensions due to its large tendency to flocculate. If not compensated for, flocculation causes inaccurate particle size analysis results by providing the sizes of particle assemblages, and not those of single particles.

Effect of particle shape on the ease of clay flocculation

Apart from the extremely small size of some clay types (<0.08 μm, section 1.5.8.1), its typical platy shape will add to the tendency of clay particles to flocculate more readily than other minerals. Upon contact, the attractional forces between two parallel flat clay surfaces are constant along the whole of their lengths (Fig. 6.1.2). However, the surfaces of other semi-spherical mineral particles curve away from each other upon contact, reducing their mutual attraction (section 1.5.5.3). It is therefore concluded that flocculation should be much higher between flat clay plates than between other sub-spherical mineral particles.

Fig. 6.1.2. Parallel borders of clay platelets aid flocculation as opposed to the cased of particles with curved borders.

Effect of high clay surface charge, and its duel nature, on the ease of its flocculation

A second reason for larger flocculation of clay particles is their high net surface charge, and its unique dual nature (section 1.5.5.1.2). The large basal surfaces have a net (−) charge. But on the clay edges, the net surface charge can vary between (+) at an acidic pH, to no charge at slightly alkaline pH (the so called point of zero charge, or p.z.c., of the edges), to a net (−) surface charge at high pH. This dual nature of their surfaces charge causes clay particles to flocculate due to edge-to-face attraction at low pH in distilled water. When, however, the pH is raised to above the p.z.c. of the edges, the clay suspension disperses due to the electrostatic repulsion between the (−) double layers now present on all surfaces (section 1.5.5.1.2).

The effect of dissolved salts concentration on clay flocculation

Along with pH, a high dissolved salt concentration is an equally important cause of flocculation. Dissolved salt depresses the thickness of the repulsive (—) double layers always present at high pH on both the basal clay surfaces and edges. These double layers consist of a higher concentration of cations (counter ions) always present in close proximity of negatively charged particle surfaces when suspended in polar liquids (section 1.5.5.1.2). When higher salt concentrations cause 'thinner' repulsive double layers, particles can move close enough to each other for attractional van der Waals forces to take over. Thus clay particles flocculate at

high enough salt concentrations, despite repulsive double layers at high pH. Even in the presence of chemical deflocculants, with small amounts of salt present: there is still some flocculation (section 4.1.1).

Effect of heat on clay flocculation

Heating a clay suspension is a fourth cause of flocculation, since it also depresses the repulsive double layers (section 1.5.5.1.2).

Effect of solid concentration on clay flocculation

The fifth cause of flocculation is a high solid concentration. The probable cause for this is that the increase in solid concentration increases the total amount of (—) surface charge. Hence, as the amount of particles increases, they will increasingly attract the limited amount of cations in solution to their basal double layers. This will decrease the amount of counter ions available to all double layers, causing all of them to become thinner. As a consequence, in distilled water, flocculation is enhanced even at a pH above the p.z.c. of the clay edges (sections 1.5.5.1.2 and 4.1.2.3.1).

In summary: the factors governing clay dispersion

From all the above it is clear that the suspension-conditions favouring better dispersion in distilled water are the following:

- low salt concentration
- the same surface charge all-round at high pH (at least higher than that at the p.z.c. of the clay edges, which is just over pH 7)
- low temperature
- low solid concentration

<u>Approach to attain effective deflocculation of clay suspensions</u>

Even when all the above four conditions are met, *complete* deflocculation of a kaolinite suspension in distilled water was not obtained in practice (section 4.1.2.3.1). To achieve complete deflocculation under these conditions, the added application of chemical deflocculants is necessary (section 1.5.5.2). Deflocculants are sodium polymeric salts that, in water, dissociate into Na^+ cations and negatively charged poly-anions. When the (–) polymer ions chemisorp on the clay edge surfaces, the (+) surface charge is reversed to (–). Thus is formed a single (–) double layer on all clay surfaces. Hence, due to all-round repulsion, the

unique edge-to-face associations causing flocculation are broken up. Since the negatively charged polyanions increase the (—) surface charge all round, the double layers are now much wider than without. Therefore, the suspension is deflocculated much more effectively than when only applying desalination and high pH.

Finding the optimum conditions for chemical deflocculation

Dispersion with chemical deflocculants is further improved by prior desalination (section 4.1.1), and also by increasing the pH to 9.5 by the addition of small amounts of Na_2CO_3 salt (sections 1.5.5.1.2 and 4.1.2.2).

At low, or no salt content, the adsorbed deflocculants polymer chains usually form loops and tails extending into the surrounding solvent. Loops and tails aids dispersion due to their resistance against compression, along with steric repulsion between them (section 4.1.2.1). Hence, apart from widening the repulsive double layers, desalination increases the efficiency of deflocculant dispersion (sections 1.5.5.2 and 4.1.1).

Furthermore, adding a small amount Na_2CO_3 produces free OH^- due to CO_3^{2-} hydrolysis, which assist in deflocculation (section 1.5.5.1.2). The OH^- ions firstly reverse the (+) edge charge to (–), assisting the deflocculant anions to facilitate edge-face repulsion. Additionally, the extra Na^+ exchanges with Ca^{2+} in the double layers.

By furthermore adding Na_2CO_3 to a clay suspension in the presence of a deflocculant, the exchange of Ca^{2+} in the double layers by Na^+ is enhanced (section 4.1.2.2). Replacing Ca^{2+} by Na^+ widens the double layers, aiding deflocculation (section 1.5.5.2). Na^+ exchange is enhanced, firstly, due to the removal of Ca^{2+} from solution through strong complexation by dissolved deflocculant polyanions. Na^+ exchange is also aided when OH^- removes H^+ from clay surfaces, freeing exchange sites for Na^+ adsorption.

In summary: apart from the edge charge reversal by chemical deflocculants, and the increase in pH when adding Na_2CO_3, the exchange of Ca^{2+} by Na^+ widens the double layers. The combination of all of these effects improves clay suspension stability.

Rather use distilled water during centrifugal washing than polar organic liquids

Should desalination be accomplished by centrifugal washing with polar organic liquids (*i.e.* ethanol, methanol and acetone), then particle size analysis should only be attempted after evaporating them completely. Otherwise, remnants of the polar liquids will cause some degree of flocculation, despite the use of a deflocculant (section 4.1.1.1).

Distilled water, heated to 80 °C and with the pH reduced to 5.0 with HCl, can be used during centrifugal washing in place of organic polar liquids. Although heating of the suspensions takes an extra 10 — 15 min. longer per centrifugal washing, it needs less washings, and gives as effective desalination as polar organic liquids.

Hydrolysis of deflocculants by the chemically active clay surfaces

The highly chemically active clay surfaces can catalyse hydrolysis of some of the deflocculants used for clay dispersion. When ageing kaolin suspensions deflocculated with TSP and Calgon, hydrolysis leads to flocculation after 9 weeks and 15 weeks respectively (sections 1.5.6 and 4.2.3.1). Hence, Calgon and TSP samples cannot be stored for longer than that before analysis is conducted.

When hydrolysis starts to take effect, visual signs appear in storage bottles (section 4.2.3.1). As soon as that happens, stored samples should be discarded. These first signs of instability are as follows:

- After 2 weeks of standing, the clay/water interface suddenly drops from about $^1/_3$ below the water level, to $^2/_3$ below. In addition, the interface becomes sharp, where usually it has a hazy upward decrease of particle concentration.
- The sample suspension, after being shaken, for the fist time stick to the sides of storage bottles. The suspension layer on the bottles' insides typically exhibited small rivulet-shaped streaks due to dewatering.
- The more the samples subsequently become unstable, the easier it becomes to re-suspend all sediments from the bottom of the storage bottles through shaking.
- Simultaneous with these three signs, the analyses result exhibit its first notable rise in cmp on the Sedigraph plotter output, but still has a smooth graph. When instability due to hydrolysis starts, the accuracy of the smallest particle sizes is affected first. Thereafter, as flocculation advances over time, the cmps of larger and larger particles begins to become inaccurate (section 4.2.3.1).

When full instability sets in, the plotter graph now suddenly exhibits large variations in cmp of between ± 1.5% and 3%, and stays at the vertical at an average of about 95% cmp.

However, with Dispex and Floccotan, hydrolysis does not take place (tested for up to 6 months of storage). Dispex and Floccotan are therefore the preferred deflocculants if samples must be stored for re-analysis over extended periods of time.

Potential negative effects of chemical dissolution pre-treatment on clay minerals

Dissolution pre-treatment is used prior to particle size analysis to break up aggregates in to single particles. This is accomplished by selective removal of cementing materials such as gypsum and other soluble salts, MnO_2, Ca- and Mg- carbonates, and iron and aluminium oxides and hydroxides. These methods, however, can have the following detrimental side effects on the accuracy of clay particle size analysis (section 1.5.7.2):

- chemical dissolution also removes the above minerals when present as separate grains in clay samples, modifying their particle size distributions;
- it may also dissolve some of the crystalline clay fraction, artificially reducing particle sizes;
- H_2O_2 treatment exfoliates vermiculite, causing its flotation on water, and its removal during subsequent centrifugal washing;
- humic substances and free organic material increase the stability of kaolinite; montmorillonite, and illite suspensions – hence, when removed with H_2O_2 treatment, will give soil particle sizes different from that in the natural environment;
- the citrate-bicarbonate-dithionite method removes some of the inter-layer aluminum material from smectites and vermiculite, resulting in greater expansion in water, and collapse upon K-saturation.

However, when not using dissolution pre-treatment, accuracy will be affected even more when aggregates remains. Therefore, to safeguard accuracy, it must first be determined which binding agents are present. Then only, the appropriate chemical pre-treatment must be applied as mildly as possible.

Combining grinding, ultrasonic treatment, and chemical dissolution of clay minerals

Clay samples need to be ground in mortar and pestle before particle size analysis, to partially break up agglomerates, and thus facilitate accurate weighing and homogenisation. After suspending ground samples, chemical dissolution of binding materials and ultrasonic treatment is normally used to further break up both the softer *agglomerates* (bound by van der Waals forces and salt bridges) as well as the tougher *aggregates* (bound by mineral cements) into single mineral particles.

The need for caution during grinding and ultrasonic treatment

When both grinding and ultrasonic treatment are conducted for too long, and too energetically, the sizes of single particles will be reduced artificially due to delamination, and

crystal breakage perpendicular to basal faces (sections 1.5.7.3 and 4.1.3.1). This must be reduced to a minimum firstly by grinding softly, and by adding enough clay to the mortar to always have at least 2 mm of clay powder between the hard surfaces of mortar and pestle.

Ultrasonic treatment with the stronger ultrasonic probe can damage clay crystals, and reduce particle sizes (section 1.5.7.4). It was, however, determined that the ultrasonic bath used during this study did not produce enough single particle break-up to be noticeable in the analysis results – even at 1 µm (section 4.1.3.1). An ultrasonic bath can therefore safely be used in combination with light grinding.

Reason to combine grinding with ultrasonic treatment

It must be kept in mind, though, that even heavy grinding cannot break up all the less resistant kaolinite agglomerates, nor the tougher aggregates (section 4.1.3.1). However, on its own, treatment in an ultrasonic bath can achieve de-agglomeration in most cases, but not all – it needs to be preceded by grinding to produce complete de-agglomeration. De-aggregation by ultrasonic bath treatment also improves when preceded by grinding. This shows that when light grinding precedes ultrasonic bath treatment, it weakens agglomerates and aggregates, substantially improving their break-up under ultrasonic treatment (section 4.1.3.1). Hence, light grinding in mortar and pestle of dried samples should always precede ultrasonic bath treatment.

Necessity to precede grinding and ultrasonic treatment with chemical dissolution treatment

On its own, only ultrasonic probes are strong enough to break up most of the tougher soil aggregates. However, with *ultrasonic probes*, the high ultrasonic energy and long durations needed to destroy the more resistant aggregates can noticeably modify particle sizes of single crystals (section 1.5.7.4). Delamination and cavitation erosion of particle surfaces can reduce the sizes of larger particles, and increase the amount of smaller ones. In contrast, larger particle sizes can also be caused by ultrasonic treatment due to agglomeration, phase changes, and increased swelling. *Ultrasonic bath* treatment, though, does not decrease the sizes of single particles in the same way during the proposed 3 min. duration of treatment (sections 1.5.7.4 and 4.1.3.1).

However, the more resistant aggregates (bound by cementing materials) could not be broken up by ultrasonic baths, even when combined with prior grinding (sections 4.1.3.1 and 4.1.3.2.2). Hence, if only grinding and ultrasonic bath treatment are used, then the subsequent particle size analysis results will give accurate single particle sizes. Therefore, along with

ultrasonic bath treatment, chemical dissolution should additionally be used to break up the most resistant aggregates — it is more effective, and causes less crystal damage than ultrasonic probes (Arustamyants, 1991).

The need to follow chemical dissolution with ultrasonic bath treatment

If the samples are kept wet between dissolution treatment and analyses, then mild ultrasonic treatment in an ultrasonic bath must follow it prior to analysis. Ultrasonic bath treatment is a necessity to break up the remaining softer agglomerates. These form due to van der Waals bonding caused by particle compaction during the subsequent centrifugal washing (used for removal of soluble salts after dissolution treatment).

Alternatively, samples may be dried and ground after dissolution pre-treatment, to enable accurate weighing in order to secure more accurate solid concentrations. But then, even more agglomerates will be formed due to salt bridges. Hence, to improve accuracy after dissolution treatment — with or without drying — a 3 min. ultrasonic treatment in an ultrasonic bath will always be necessary to break up any newly formed agglomerates after dissolution treatment (section 4.1.3.1).

When comparing the results of different analysis, and their grinding and ultrasonic treatment are not conducted at standard durations, then *repeatability* and *reproducibility* will also suffer (section 4.1.3.1). However, experimental error-results had shown that differences in the intensity of grinding are the larger control to the size of errors – even larger than those caused by discrepancies in ultrasonic time (section 4.1.3.1). Therefore, since the intensity of grinding is impossible to duplicate, comparability between different operators might be impossible to attain. Hence, the proposed use of chemical dissolution plus ultrasonic treatment, rather than grinding plus ultrasonic treatment will, apart from benefiting *accuracy*, additionally also benefit *repeatability* and *reproducibility*.

Correct procedure for ultrasonic treatment to ensure repeatability, and comparability

When ultrasonicating samples, the following four facts must be kept in mind to ensure repeatability, as well as the comparability between different operators:

Firstly, raising the ultrasonic time in an ultrasonic bath initially leads to increasing cmp values – especially in the smaller particle sizes – and then remains constant (section 4.1.3.1). This implies that to insure reproducibility, and therefore also comparability between different operators, ultrasonic time needs to be standardised.

Secondly, soaking before ultrasonic treatment improves the break-up of agglomerates. An overnight soaking was found to be enough to ensure this for all kaolinite types tested (section 4.1.3.2.1 and 4.1.3.2.2).

Thirdly, it is the total amount of ultrasonic energy over time that determines the complete break-up of agglomerates and aggregates (section 1.5.7.4). Therefore, to ensure comparability between different operators, their ultrasonic baths do not need to have the same watt rating. Each, however, need to determine the correct minimum ultrasonic time for his own specific ultrasonic bath.

The latter can be accomplished by a series of once off re-analysis of a few samples of different clay and soil types with increasing ultrasonic time. When this is done, two plateaus in cmp are observed with increasing ultrasonic time (section 4.1.3.1). The development of the first plateau is interpreted as the break-up of the softer agglomerates, while the development of the second plateau is seen as the destruction of the tougher aggregates. The average time for a specific ultrasonic bath to reach the first cmp plateau can thereafter be taken as the standard ultrasonic time to break up all of the softer agglomerates remaining after dissolution treatment.

All tougher aggregates, though, are broken up by the dissolution of mineral cements — hence, with dissolution samples only a first plateau should form. Only the mild ultrasonication time at the start of this first plateau is necessary to break up all softer agglomerates remaining after dissolution treatment (formed during subsequent centrifugal washing and drying). In this way particle damage due to all pre-treatments is kept to a minimum.

Combining grinding in mortar and pestle with chemical dissolution and ultrasonic treatment

In summary therefore: grinding and ultrasonic treatment are not totally effective to break up the tougher aggregates formed by mineral cements. Hence, chemical dissolution treatment must be used to remove all cementing materials, thus destroying all aggregates. Ultrasonic treatment then should follow it, to break up the softer agglomerates forming during the centrifugal washing and/or drying that always follows on dissolution treatment. Light grinding should be used only to facilitate accurate weighing where applicable.

Each of these three pre-treatments, though, can damage clay crystals, and thus modify the natural particle size distribution (sections 1.5.7.2, 1.5.7.3, 1.5.7.4). However, the combination of all three allows the break-up of all agglomerates and aggregates — and additionally, their combined use also allows that mild treatment of each has the desired effect. Thus, the combination of mild grinding, chemical dissolution, and ultrasonic treatment will affect

optimum de-agglomeration and de-aggregation, but will still keep crystal damage to a minimum (section 4.1.3.1).

Deflocculants enhance agglomerate break-up during ultrasonic treatment

The addition of deflocculants assists the break-up of clay agglomerates during energetic stirring, shaking, or ultrasonic treatment of a suspension (sections 4.1.3.2.1 and 4.2.3.1). Hence, a deflocculant must immediately be added to clay suspensions when they are first made up with water. Dispex is best to promote de-aggregation, followed closely by TSP and Floccotan, with Calgon a bit further back.

Additional ultrasonic treatment not necessary to affect resuspension after long storage

When re-analysis is done after an extended storage in the wet state, samples do not need to be ultrasonicated again: only shaking is enough to completely re-suspend the deposited clay, and still secure excellent repeatability (section 4.2.3).

Dangers of using ball or oscillatory mills prior to particle size analysis

In place of the mortar and pestle, clay minerals should never be milled in a ball or oscillatory mill prior to ultrasonic treatment (sections 1.5.7.3). Milling in these devices delaminates, and breaks the clay particles to cause smaller particle sizes. Conversely, milling in these devices can even lead to *larger* particle sizes due to aggregation. Such high-energy pulverization can also break, and crush the outer crystal structures of kaolinite and pyrophyllite along their basal planes, causing collapse when stored a few days under dry conditions. All of these effects should reduce both accuracy and reproducibility.

The steps to ensure optimum dispersion of clay suspensions

With all the above in mind, the following is suggested as standard clay dispersion procedure:

- all dry samples should first be lightly ground (sections 4.1.3.1 and 4.1.3.2.1),
- conduct dissolution treatment, followed by desalination with centrifugal washing in water only (heat to 80 °C, and reduce pH to 5.0 to facilitate deposition — sections 1.5.7.2, 4.1.1, and 4.1.1.1),
- soaked at least overnight at a 0.7% Dispex concentration (sections 4.1.3.2.2 and 5.1),
- only then ultrasonic bath treatment can be given for the average time for the specific ultrasonic bath to the first cmp plateau (section 4.1.3.2.2).

Kaolinites should not be ultrasonicated for too long past the determined standard ultrasonic time. This may in some cases lead to re-agglomeration; hence, accuracy will be sacrificed (section 4.1.3.2.2).

6.2 EVALUATING THE VALIDITY OF USING SEDIMENTARY PARTICLE SIZE ANALYSIS RESULTS OF SWELL-CLAYS TO CHARACTERISE THEIR NATURAL ENVIRONMENTS

As seen above, sedimentary particle size analysis is normally conducted on de-aggregated and de-agglomerated clay suspensions, which are also desalinated, and chemically dispersed with a deflocculant at high pH. None of these conditions exists in nature. Hence, such particle size analysis will not at all reflect the particle size distribution of any natural situation.

Moreover, when swell-clays are present in their natural environments in soil, in suspension in natural waters, or in a soft sediment, a large amount of physical and chemical factors determine their particle sizes. Yet again, most of these conditions cannot be reproduced during any particle size analysis method.

With the above in mind, the relevance of using sedimentary particle size analysis results of swell-clays to characterise their natural environments will be evaluated next, by using a few examples. First, though, the factors controlling the particle sizes of smectites and mixed-layered clays must be summarised.

The amount of swelling, and therefore the particle size, of swell-clays depends on:

- amount of isomorphous substitution, and therefore the clay type (section 1.5.8.2.5)
- type of exchangeable inter-layer cation (-s) (section 1.5.8.2.1)
- whether in water or in air:
  - when in *air*, swelling additionally depends on
    - the relative humidity (section 1.5.8.2.1)
    - in soil: the temperature and accompanying relative humidity (section 1.5.8.2.7)
  - and when in *water*, swelling additionally depends on:
    - the concentration of any cation in solution (sections 1.5.8.2.1 and 1.5.8.2.3),
    - solid concentration of the suspension (section 1.5.8.2.4),
    - pH of the suspension (section 1.5.8.2.3),
    - the presence, or not, of a deflocculant (section 1.5.8.2.2)

- in both in air and in water, outside pressure affects the swelling (section 1.5.8.2.6), and is controlled by:
    - when in soil: pressure is controlled by the depth of overburden and, the depth below the water table, and restriction to swelling and therefore also compaction and porosity,
    - when in air: the force opposing swelling is exerted by air pressure

The amount of unit-layers of swell-clays in suspension, and hence also the particle size, depends on:

- the type of exchangeable inter-layer cation (section 1.5.8.3.1)
- concentration of exchange cations in solution (section 1.5.8.3.1)
- solid concentration (section 1.5.8.3.2)
- external pressure, and pressure history of the suspension (section 1.5.8.3.3)
- duration of ageing of the suspension (section 1.5.8.3.4)

Most of the last-mentioned factors therefore have opposite effects on the amounts of swelling than they will have on the amounts of unit-layers:

- *type of exchange cation*: swelling is generally less for exchange cations that cause larger amounts of unit-layers.
- *decrease in salt concentration*: swelling increases, whereas the number of unit-layers decreases.
- *decrease in solid concentration*: swelling increases, whereas the number of unit-layers decreases.
- *decrease in external pressure*: swelling decreases, whereas the number of unit-layers increases.

From the above it is firstly obvious that when trying to experimentally determine what the particle sizes of clay will be when it is in *soil*, in *unconsolidated sediment*, or when *suspended in a river or a lake*, then all the above chemical and physical conditions must be the same during the analysis as in the natural situation — which in most cases is impossible. It is, furthermore, not always possible to determine which of these factors has an influence on particle size in the natural situation, and what is its magnitude.

To practically illustrate the non-validity of using an analysis result to reflect the true particle size distribution in a natural situation, the following few examples are given:

Effect of swelling, and variation of the amount of unit-layers, during soil particle size analysis

When soil pores are not filled with water, the swelling, and therefore the particle size, will continually adjust to changes in the pore ambient moisture content. But, sedimentary particle size analysis is mostly conducted in water. Therefore, it is clear that in water with a deflocculant, sedimentary particle size analysis will give a single swollen particle size distribution that can differ greatly from the diverse particle sizes it can have when in dry soils with varying humidities — compare Tables 1.5.8.2.1(a) and 1.5.8.2.2 (a), (*swelling in air*) with Tables 1.5.8.2.1 (b) and 1.5.8.2.2 (b) (*swelling in water*).

The magnitude of the discrepancy between particle size determined in water and the different particle sizes sell-clays can have in soil will furthermore be determined by the combination of any of the following factors.

- the difference between the salt concentration of the exchangeable cations during analysis (normally desalinated) and that in the natural invironment (vary greatly);
- the difference between pH of the analysis and that in nature (mostly acidic in nature, but alkaline by choice during analysis);
- the presence, or not of a deflocculant during sedimentary particle size analysis;
- the solid concentration of the analysis as compared to that in nature;
- the temperature and specific ambient moisture content in the soil;
- the amount of swell-clays present in a mixture, the interlayer cation, and hence the difference between the swollen densty of each swell-clay component and the average clay density used to calculate the esd;
- the relative amounts of swell-clays present in mixtures, and hence the amount of mixed-layered clays produced by the agition during sample preparation and analysis.
- the amount of clay close to and below 0.65 μm, and hence the magnitude of the effect of Brownian diffusion;
- the amount of montmorillonite below 0.01 μm, and hence the magnitude of the effect of inevitable flocculation;

It is obviously impossible to have all of these the same in dry soil as during analysis.

When, on the other hand, the soil is *saturated with water*, the particle sizes of swell-clays determined by sedimentary particle size analysis may also differ from it – even when size analyses are determined in water at the same pH and salt content. Discrepancies between analyses results and the true particle sizes may be caused by:

- the limitation of swelling by soil overburden pressure,
- space restriction to swelling,
- the increase in soil water pressure with increased burial depth below the water table,
- much smaller solid concentration during analysis,
- and lack of ageing after sample preparation (2.5x decrease in thickness after 4 months of ageing — section 1.5.8.3.4).

Further complications related to swelling and change in the amount of unit-layers after dilution of solid concentration prior to analysis

The effect of change in solid concentrations in preparation to sedimentary particle size analysis of swell-clays adds further complications related to swelling and the amount of unit layers. As a clay suspension is diluted for sedimentary particle size analysis, both the solid concentration and the salt content will decrease. This leads to the reduction in the amount of unit-layers (section 1.5.8.3.2).

However, dilution of the salt concentration will simultaneously increase the swelling, which, if it is H^+, Li^+, Na^+-montmorillonite, will dominate over the decrease in the number of unit-layers, and tend to *increase* the particle size (1.5.8.3.1). Contrarily, during dilution of Ca-montmorillonite suspensions the decrease in the amount of unit-layers will dominate over swelling, and in this case increase the particle size.

The balance of these effects will yield different particle sizes for the same sample when diluted to different solid concentrations. Both the Andreasen and centrifugal methods are conducted at solid concentrations more than 6x lower than that stipulated for the Sedigraph. Therefore — apart from lower Brownian diffusion and hindered settling with the former methods — due to the larger dilution of their suspensions, their particle size results for swell-clays and mixed-layered minerals will differ from that of the Sedigraph.

Therefore, in order to compare the results of swell-clays between the different sedimentary particle size analysis methods, it is important to analyse them at similar, low solid concentrations. The preferable solid concentration (low enough to reduce hindered settling to

levels that will ensuring accuracy) lies between 0.4% and 1.0% by volume.

Effect of swelling, and variation in the amount of unit-layers, during soft sediment analysis

When the particle sizes of clay sediments in riverbed sediments are determined, it will not necessarily give the same particle size as during deposition.

In equilibrium with air CO_2, natural waters are acidic (pH 5.6), and will always have some salt present. Under these conditions, all natural clays will be flocculated (section 1.5.5.1.2). Exceptions, though, might be found in areas rich in carbonaceous rocks. Here, high enough pH values may exist, which will help to deflocculate clay particles. However, neither the pH, the exchange cation, the salt and solid concentrations, nor the age of the suspension during deposition will necessarily be known.

Hence, even if the particle size analysis is conducted without a deflocculant, the exact physical and chemical conditions during deposition cannot be duplicated during sedimentary particle size analysis. Therefore, the results of any method of particle size analysis will always differ from that during deposition.

The significance of swelling, and the change in the amount of unit-layers for hydrodynamic calculations

Swelling, and the change in the amount of unit-layers, will therefore compromise the application of sedimentary methods for one of its potential uses in sedimentology. Firstly, the particle size will not be the same during the analysis as in the natural situation because of the last-mentioned reasons. Secondly, a different amount of swelling will additionally causes the density during the analysis to be different from that during deposition. Hence, the clay particle size determined with a sedimentary method cannot necessarily be used along with hydrodynamic equations to accurately calculate the conditions during deposition, and thus to validly characterize the sedimentary environment (see also the introduction of Chapter 1 and section 1.5.4). This is contrary to the case with sand sized grains, which are not effected by any of the abovementioned factors acting on the much smaller clay particles.

From the above few examples it is concluded that in most cases when swell-clays are present in samples, then the results obtained by any particle size analysis method will not by far reflect the natural situation.

However, if the sedimentary analyses of clays are conducted as-is on a natural clay *suspension*, the results should give the actual sizes of either its flocks or single particles

(depending on the pH of the natural water) (see section 6.3).

The inherent inaccuracy of clay mixtures, especially when containing swell-clays

The flocculation of very small swell-clay particles < 0.1 μm, and the effect of Brownian diffusion close to the lower size limit of sedimentary methods, should cause the same inaccuracy in the small fraction of clay mixtures as in single clays (sections 1.5.1.1.2, 1.5.1.2 and 1.5.5.2.1).

Inaccuracy caused by the low density of swell-clays in water when present in clay mixtures

With clay mixtures, the low densities of swell-clay in water cause two additional accuracy problems. The densities of the swell-clay components of a mixture can differ hugely from the average density used to calculate the scan rate of the Sedigraph, or to calculate the esds during the other sedimentary particle size analysis methods (section 1.5.8.2, and 1.5.10). This is especially the case with the large swelling H, Li, and Na-varieties of montmorillonite). The more the densities of a component differs from the average density, the inaccurately wider the particle size distribution for mixtures should become. For the same reason, the particle size distribution containing the less dense swell-clays shifts to larger cmp values. Both these results since the less dense components have lower settling velocities than required by the scan rate (which is calculated for a higher density) (section 1.5.10, and Table 1.5.10.1). Therefore, it is very important to find the correct average density value of a mixture.

Using 2.65 g/cm^3 as average density for esd calculations duringsedimentary particle size analysis

The normally used average density value (2.65 g/cm^3), does not take into account the relative amounts of the clay components of the mixture (section 1.5.10). The relative amount of each clay type in a mixture is characterised by its volume fraction, which varies widely according to the respective particle densities. Therefore, when using the standard, fixed 2.65 g/cm^3 as the density for a clay mixture when containing (say) very low density Na-montmorillonite (1.034 g/cm^3), it will cause the esd for the Na-montmorillonite component to be calculated much smaller than it really is. This error enlarges as the percentage of the mineral fraction increases whose density differs most from the chosen average density of 2.65 g/cm^3 (section 1.5.10, and Table 1.5.10.1). When using 2.65 g/cm^3, the error in cmp can vary with anything between –1.5% cmp for Ca-montmorillonite, to 6.3% for Na-montmorillonite — depending on the relative amount of the swell-clay in the clay mixture.

Hence to secure more accurate sedimentary particle size analysis results, the volume fractions of each component of a mixture must be used to calculate the average density. However, to calculate the volume fractions, the quantitative XRD analysis of each mixture needs to be conducted prior to its particle size analysis (section 1.5.10).

Effect of low swell-clay density on X-ray sedimentometer accuracy

Clay minerals in mixtures that have different densities have different X-ray mass absorption coefficients, which can noticeably affect the accuracy of the Sedigraph (section 1.5.10). The error in cmp will be over 1% if the component with the smallest mass absorption coefficient is over 5%, or when the component with the larger mass absorption coefficient is over 1%.

In summary therefore: swell-clays, when present in *clay mixtures*, will always cause inaccurate results for all sedimentary methods due to the problems caused by small particle size, low density, large density differences with non-swelling components, and a lower mass absorption coefficients.

Effect of the flocculation of clay mixtures on accuracy

A last problem for clay mixtures is caused when enough salt is present to result in flocculation (even in the presence of a deflocculant). When differences in clay surface charge density are large enough, then different clay species will be flocculated selectively at different salt concentrations. When, furthermore, the salt content of a clay mixture is decreased, smaller particles go into suspension first (montmorillonite) through spontaneous deflocculation, while larger ones will still stay flocculated. The order of flocculation is: vermiculite > illite > kaolinite (section 1.5.8.3.1). From this it is concluded that during particle size analysis, different salt contents should give differing size distributions to the same natural sample when consisting of a mixture of clay species.

Effect of varying salt concentration on the particle sizes of mixed-layered minerals

Furthermore, since different types of *mixed-layered minerals* will form at different salt and solid concentrations, and small flocks deflocculate first when lowering the salt concentration, it is concluded that *diluting* a suspension of a clay mixture to different solids contents, may cause different particle sizes due to selective flocculation into different mixed-layered minerals.

Along with the effect of the increased swelling with decrease in salt concentration, the

combination of all the last-mentioned effects will therefore cause a complex change in particle size distribution for different dilutions of clay suspensions.

Hence, the particle size distributions of mixed-layered minerals should differ between the Sedigraph and the Andreasen method also due to the dilutions of salt concentration when making up different solid contents (3.85% and 0.5% solids concentrations respectively). Due to salt concentration dilution, performing a particle size analysis with the Sedigraph should therefore give a narrower particle size distribution than with the Andreasen pipette method due to the removal of smaller particles to form larger flocks. It should also give larger particle sizes at any cmp value. This further underlines the need for a fixed standard solid concentration for all sedimentary size analysis methods.

Further problems posed to accuracy by mixed-layered clay minerals

Barring small particle sizes, interstratified clays in a mixture will cause the same already mentioned problems encountered by single swell-clays. It is suggested that when they are part of a mixture, interstratified clays will have almost the same negative result on the accuracy with all the sedimentary methods.

Mixed-layered clays, furthermore, generally have significantly larger particle sizes than single clay mineral species, and might therefore additionally be larger than the upper size limit for accurate sedimentary particle size analysis (49.6 μm).

Artificial formation of mixed-layered clays during sample preparation

Mixed-layered clay particles can be formed in rock by natural processes. However, it can also be artificially produced in a manner that should be very significant to the accuracy of all particle size analysis methods. Suspensions consisting of mixtures of illite plus swell-clays (especially the Ca- and Na- forms of montmorillonite) can be transformed into mixed-layered minerals through agitation during sample preparation (section 1.4.9). Swell-clays delaminate, and recombine into new mineral particles containing a different stacking order of unit-layers of different clay types. This may especially happen with the Na^+ or Li^+ forms of montmorillonite due to their large swelling, causing weak inter-layer bonding. Mixed-layered clays have *much larger particle size than its original mineral components.*

Since energetic agitation during dissolution, desalination, and during the analysis itself can not be avoided, it is surmised that clay mixtures containing swell-clays will always yield larger particle sizes, and different particle size distributions after sample preparation than while still

in their natural condition.

Secondary clay deposits, of course, will already have gone through an agitational phase due to erosion. But different mixed-layered minerals may still form during sample preparation especially due to the necessary dilution of salt content. The largest change in particle size distribution due to mixed-layered formation should be encountered by sample preparation of *in situ* clay mixtures containing swell-clays and clays like illite, chlorite and, to a lesser extent, kaolinite.

The effect of the suspended clay on the density and viscosity of the suspension liquid

The density and viscosity of *distilled* water is normally used to calculate the scan rate of the Sedigraph, as well as the esds of the Andreasen method.

Clays have large anion exchange capacities, and will therefore require much more deflocculant molecules than other minerals to affect optimum dispersion. Consequently, their suspension liquids should differ enough in density and viscosity from that of water to give inaccurate results when their scan rates are calculated with that of distilled water. Tests conducted during this study show that due to the practice of using density and viscosity of distilled water to calculate scan rate, the results with *kaolinite* suspensions can be inaccurate with between 1.77% and 5.01% cmp (section 4.2.1.3).

Similarly, other tests also showed that the clean deflocculant solution at 0.7% concentration should rather be used to adjust the 0% setting of the Sedigraph (section 4.2.1.4). When using a clean deflocculant solution at 1.5% during a test, a cmp error of only 0.5% was caused, instead of a 1.5% error when distilled water is used for this purpose.

However, illite and swell-clays have much larger anion exchange capacities than the above-mentioned kaolinite (van Olphen, 1977). It can therefore be expected that illite and swell-clays will potentially remove much more deflocculant molecules from suspension than kaolinite. Therefore, for most soils the error when the density and viscosity of the water is used for scan rate calculations should be less than those of kaolinite given above.

Experimental determinations of density and viscosity are very time consuming. It is therefore not worthwhile to determine the density and viscosity of the suspension liquid of each soil/deflocculant combination before analysis with a sedimentary method. To save time, the density and viscosity of the suspension liquid of a clay giving the average error should be determined over the temperature range of the Sedigraph. Thereafter, in place of the density and viscosity of water, it can be used with all clay samples for scan rate calculations with the

Sedigraph, or for esd calculations with the Andreasen method (see the suggestions for further study of section 4.2.1.4). The same liquid can then be retained, and also be used during all subsequent 0% adjustments of the Sedigraph.

The errors caused by this approach will be much less than with the conventional approach of using the density and viscosity of distilled water.

6.3 THE CORRECT APPROACH TO SEDIMENTARY PARTICLE SIZE ANALYSIS OF CLAYS

To ensure comparability between different operators, as well as accuracy and reproducibility, a standard method needs to be designed to keep all of the material-related parameters the same, and at an optimum, to ensure complete dispersion.

Deciding which dissolution pre-treatment to use

When deciding to obtain the *single particle sizes* of any unknown clay sample, the first step must always be to test which dissolution pre-treatment is necessary (section 1.5.7.2). Then conduct only the appropriate dissolution treatment as mild as possible to reduce single crystal damage as far as possible. Thus possible artificial modification of the particle size distribution is reduced to a minimum.

It must be noted that if dissolution is omitted, then the subsequent particle size analysis can potentially give sizes representative of the natural situation, provided that it is conducted under the natural physical and chemical conditions. Without chemical dissolution, cementing material will, amongst others, cause the same restriction to swelling and shrinkage during analysis as in its natural condition. The soil sample will also contain the same amount of aggregates and free amorphous minerals and oxides in its particle size distribution during analysis as in its natural condition.

Quantitative mineralogical analysis to ensure accuracy of clay mixtures

Dissolution treatment is followed by a qualitative XRD analysis to establish which swell-clays are present. This is necessary to calculate the accurate average density for a clay mixture for use in scan rate calculations with the Sedigraph, or the calculation of settling times with the Andreasen method (section 1.5.10).

If any swell-clays are present, the individual samples need to be exchanged to a standard cation-form. This is firstly to secure the same amount of swelling, and therefore standard densities of swell-clays during analysis. This will provide comparability between different

samples (reproducibility), and also between different operators (comparability).

Exchange with the same cation will further ensure the same number of unit-layers for swell-clays. This will ensure comparable particle sizes between different samples when conducted by the same operator, as well as between different operators.

Correct way to calculate the average density of clay mixtures

With the mineralogical content of a clay mixture and the cation form now secured, the density of each swell-clay component must be calculated for the stipulated exchange cation in the presence of the same deflocculant (section 1.5.8.4.2). The calculated densities of individual swell-clay components are then used to calculate an accurate average density of the clay mixture (section 1.5.10).

Up to now, though, only the densities for Ca-montmorillonite, and Na-montmorillonite *in the presence of Dispex* deflocculant have been calculated from Monte Carlo data (*viz.* 3.00 g/cm^3 and 1.0337 g/cm^3 respectively). Therefore, it is recommended that all size analyses of mixtures containing swell-clays be conducted only after cation exchange with either NaCl or $CaCl_2$. Because the particle sizes of Na-type swell-clays are substantially different than their Ca-variants, the exchange cation type must be stated along with the results.

The density of mixed-layered minerals with different exchange cations in the presence of Dispex (found to be the best deflocculant) must still be determined in the same manner as for Ca- and Na-montmorillonite (sections 1.5.8.4.2 and 1.5.8.2.2).

Desalination by centrifugal washing is to be conducted only with distilled water

After cation exchange, the excess exchange cation must be removed to prevent flocculation during the subsequent particle size analysis. It can be accomplished either by dialysis or centrifugal washing (preferable since it is much faster) (Kunze and Dixon, 1986). If centrifugal washing is employed, it must be conducted by repeated washings with water. To facilitate shorter centrifugal times, the suspension can be flocculated by reducing the pH to 5.0 with HCl, and heating the suspension to at least 80 °C. Centrifugal washing is repeated until 0.01 M $AgNO_3$ shows no traces of Cl^- (section 4.1.1.1), or till the salt concentration had fallen to below 10 m.eq/l (Kunze and Dixon, 1986). This will not only ensure that most of the original salt is removed, but also that the small amount of exchange salt that remains will not be enough to flocculate the suspension during subsequent particle size analysis (section 4.1.1). There will also not be enough variation in cation content to cause different amounts of unit-

layers, or different degrees of swelling of swell-clay particles (section 1.5.8.2.1; Tables 1.5.8.2.1 (a) and (b), and Tables 1.5.8.2.2 (a) and (b)).

If cation exchange is not conducted, but the clay is analysed *for sizes of single particles*, then any natural soluble salts present should still be removed by centrifugal washing to prevent flocculation. This will additionally prevent differences in the amount of unit-layers, and unlike amounts of swelling between different samples, and ensure comparability between different operators (sections 4.1.1, 1.5.8.2, 1.5.8.3).

If the wet clay is to be analysed directly after desalination, an organic polar liquid (*e.g.* ethanol, methanol, or acetone) should not be used for centrifugally washing prior to any particle size analysis method. If the wet sediment is analysed directly after centrifugal washing with an organic solvent, its residue causes noticeable flocculation despite the use of a deflocculant (section 4.1.1.1).

The need for a standard solid concentration

Since the solid concentration influences the swelling and the amount of unit-layers of swell-clay particles, a standard solid concentration for all sedimentary particle size analysis needs to be established to allow comparison of results between operators (sections 1.5.8.2.4 and 1.5.8.3.2).

At low solid concentrations between 0.38% and 1.13% by volume, both models of the Sedigraph give the same results as the Andreasen method (Weaver and Grobler, 1981; Watts *et al.*, 2000). Furthermore, within a similar solid concentration range – between 0.41% and 1.0% by volume – both the influences of low concentration hindered settling (increase in settling velocity) and high concentration hindered settling (decrease in settling velocity) is at a minimum (sections 1.5.2 and 1.5.2.1.2). Therefore, in order to ensure accuracy and comparability, a solid concentration of between 0.41% and 1.0% by volume is suggested for all sedimentary particle size analysis methods – including for the X-ray sedimentometry methods.

This is an ideal solid concentration because it is also below the lower limit for gelling of Na-montmorillonite (1.13% solids by volume) (Watts *et al.*, 2000).

Optimum dispersion by using both chemical deflocculation and high pH

Clays must be dispersed with a deflocculant at pH 9.5 to obtain the most effective dispersion – the increase in pH to 9.5 alone is not enough to effect complete dispersion

(section 4.1.2.3). However, different deflocculants give slightly different results for different kaolinite types (section 4.1.2.1), and also give markedly different results for Ca-montmorillonite (section 5.1). Moreover, different deflocculant types cause different particle size distributions for montmorillonite, since each deflocculant affect its swelling differently (sections 1.5.8.2.2 and 5.1). Therefore, one specific deflocculant needs to be used during a standard procedure for sedimentary analysis of clays, to ensure comparability between operators.

Four deflocculants were tested for their effectiveness in dispersing kaolinite suspensions. They were: Calgon[14] (sodium hexametaphosphate), Dispex N40 (sodium polyacrylate), TSP (tetra sodium phosphate) (Fig. 1.5.5.2.1), and Floccotan Sudguard 3195 (a co-polymer between acrylic acid and 2-acrylomido-2-methylpropane sulfonic acid) (section 4.1.2.1). All four deflocculants gave similar results at 1.5% concentration, with Calgon slightly better than the rest.

Of the four deflocculants tested, Dispex N40 is recommended as standard deflocculant for clay suspensions. It is chosen above Calgon (considered here as the second choice) for the following reasons:

- Dispex gives equally effective dispersion as Calgon (Table 4.1.2.1.3);
- it gives virtually the same repeatability and reproducibility as Calgon (section 4.2.2.3);
- it is not hydrolysed with ageing as Calgon are (section 4.2.3.1);
- with Dispex, accuracy is not as sensitive to pH as with Calgon (section 4.1.2.2);
- Dispex best supports de-agglomeration during ultrasonic treatment (section 4.1.3.1).

Dispex should be used at a concentration of 0.7%, (calculated at grams Dispex as supplied, to the mass of clay). A Dispex concentration of 0.7% is enough to deflocculate the finest kaolinite (Amazone coater), but does not flocculate other kaolinite suspensions due to over-dispersion (section 4.1.2.1, and Tables 4.1.2.1.2 (a) to (d)).

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[14] *Calgon and TSP are supplied by most chemicals manufacturers. Dispex N40 is manufactured by Ciba Specialty Chemicals (www.cibasc.com), and distributed in South Africa by themselves (Tel. (011) 929 4344). Floccotan is manufactured in South Africa by Floccotan Pty. (Ltd.), Pietermaritzburg, South Africa (http://zapages.com/floccotan-1; Tel. (033) 346-923, Fax: (033) 168-422).*

The importance of a standard pH value

The pH affects the amount of swelling of montmorillonite (section 1.5.8.2.3) and the effectiveness of chemical deflocculation (sections 1.5.5.2), and therefore influences particle size analyses results of all clay types to a greater or lesser extent (section 4.1.2.2). Therefore, the pH must be the same between different analyses, as well as between different operators. A pH of 9.5 is recommended, since it ensures the most effective dispersion with all deflocculants (section 4.1.2.2), but is not high enough to lead to dissolution of clay particles.

Preventing the effect of particle size change due to ageing

To prevent ageing causing a decrease in the amount of unit-layers of swell-clay crystals (section 1.5.8.3.4) – and hence the decrease in particle size with ageing – the analysis needs to be completed directly after ultrasonic treatment and shaking.

The necessity to reproduce the natural chemical and physical conditions during analysis when natural particle sizes are required

If the particle size of any clay sample is determined by means of sedimentary analyses to characterise a specific natural situation, all the abovementioned physical and chemical conditions controlling swelling and the amount of unit-layers, as well as those affecting deflocculation, must be as close as possible during the analyses to that of the natural environment. This will ensure that esds will be as close as possible to those in the natural situation. The same applies when using any other method for particle size analysis of clays.

Since in most cases clay particles will be flocculated in natural waters, the particle sizes obtained when analysing them as-is, will actually be *flock-sizes*. However, both high pH and low solid concentration causes smaller flock sizes, since both these conditions cause smaller inter-particle forces (Katari and Tauxe, 2000). Therefore, during sedimentary analysis the required high pH (9.5) and low solid concentration (0.4% to 1.0%) therefore might in many cases cause smaller flock sizes than in natural waters. Hence, the best approach to determine the true particle size characterising the natural environment will be to determine *flock-sizes* without a deflocculant, at the natural solid concentration, and at the natural salt content and pH. In short: use the clay suspension as sampled in its natural form.

When clay size analysis is conducted at the same solid concentration as in nature, an additional benefit is that the salt concentration and content will also be the same. This guarantees the same amounts and types of the dissolved cations. In turn, this – along with the

pH and solid concentration – determines the amount of swelling, and the amount of unit-layers (sections 1.5.8.2.1, 1.5.8.2.3, 1.5.8.2.4, 1.5.8.3.1, and 1.5.8.3.2). These again control the clay particle size and density, and hence the size of the single swell-clay particle components of the flocks.

The salt concentration also plays its part to determine the density of the *flocks themselves*, by regulating the flock size and porosity. All of these determine the flocks' settling velocity, and hence whether the flock sizes determined by a sedimentary method will be the same as in the natural situation.

When, however, particle size analysis needs to be conducted at lower solid concentrations than in nature to prevent hindered settling, the supernatant of the natural suspension must be used to dilute the solids. Thus the salt concentration and composition, and therefore natural flock density will at least be retained, and the amount of swelling and the amount of unit-layers will be closer to those in nature.

To obtain the particle size of natural suspensions, both the older and newer versions of the Sedigraph can be used as alternative to the more time-consuming Andreasen method. The Sedigraph gives similar particle size analysis results when conducted at the lower solid concentration of the Andreasen method (section 1.5.2.1.3).

Acquiring flock or aggregate density to use in scan rate and settling time calculations

When analysing natural flock and/or aggregate sizes with sedimentary particle size analysis, the flock densities must be known beforehand to calculate scan rate (Sedigraph) or settling time (Andreasen method).

Flock, agglomerate, and aggregate densities of individual flocks can be determined with either a zeta-meter or a dark-field microscope with a graduated eyepiece, with both instruments turned on their sides. Such set-up will permit gravity sedimentation times of individual particle assemblages to be measured, over a known distance, under microscopic observation. From this, their correct average densities can be computed, from which to calculate the correct cell scan rates or settling times. This will enable the determination, with any sedimentary method, of particle size distribution of flocks, agglomerates or aggregates as it occurs in nature.

When all three particle assemblages (flocks, agglomerates, aggregates), as well as single particles, are present in a mixture, the densities of each must be used to calculate an average density according to the volume fraction of each (just like in the case of a mixture consisting

only of single clay types — section 1.5.10).

Measuring natural clay particle sizes in air

To find the particle size in when in air, a normal sedimentary method using liquid as the suspension medium can not be used since swell-clay particle sizes can in some cases be as much as 30x to 56x larger than in air (sections 1.5.8.2.1 and 1.5.8.2.2). In stead, air classification needs to be employed at the same relative humidity as in the natural situation. When the natural particle size is required, the analysis must be done without prior cation exchange, since different interlayer cations cause different amounts of swelling in air (section 1.5.8.2.1 and Tables 1.5.8.2.1.1 (a) and 1.5.8.2.1.1 (b)).

With most soils, though, it is doubtful whether the *single* particle sizes of their swell-clays in the dry condition can be determined accurately even by means of air classification. Dissolution methods will first have to be employed to break up all aggregates. During the inevitable agitation of the clay suspension accompanying this, the particle sizes of most swell-clays will be modified by the artificial formation of mixed-layered clay minerals.

Hence with air classification, as with clay suspensions, true dry particle sizes of clays can only be determined without prior dissolution treatment. However, without dissolution pre-treatment, most air-dried clays, like natural suspensions in water, will not only be consisting of free single particles, but will also contain aggregates and agglomerates.

Application of sedimentary particle size analysis results when the natural conditions cannot be reproduced during analysis

Even though the same particle size distribution of the natural condition will in most cases not be obtained during particle size analysis, such results can still be very useful. When a direct correlation exists between the experimental particle size distribution and a specific characteristic of soil, a suspension, or a sediment, that characteristic can still be accurately foretold from the analysis result. For instance, a soil with large cmp < 2 µm always correlate with a high clay content, which again correlate with a low soil permeability and a large water retention capacity. Despite the fact that in saturated soil the particle sizes are most likely much smaller than during sedimentary particle size analysis (due to space restriction to swelling, soil overburden pressure, and higher solid and salt concentrations than during the analysis) a good correlation still exist between the single particle sizes obtained in a sedimentary method and the soil properties described above.

The same is true in industrial applications. For example a kaolinite with a fineness of more than 80% < 2 μm always indicates it being a good paper coater. However, the kaolinite is completely deflocculated during sedimentary particle size analysis, but during paper coating it is flocculated due to binding agents.

However, for whatever purpose the results of sedimentary particle size analysis is used: to be accurately and reproducibly applied, a standard method is an absolute necessity.

6.4 PROPOSED STANDARD PROCEDURE FOR SEDIMENTARY PARTICLE SIZE ANALYSIS OF CLAYS

Since all apparatus-parameters were kept constant while investigating every aspect needed to design the standard method proposed below, it only relates to material-related properties. The proposed standard method is therefore applicable to all sedimentary methods, and deals mainly with sample preparation. The procedure of the chosen sedimentary method should be found in the handbook of the specific apparatus. Additional precautions for the older model Sedigraph 5000D can be obtained in the MS Word document, *ApparatusParameters.doc*, on the CD disk at the back-cover of this book (also to be found there is the document *Tesis2.doc*, which is a soft copy of this thesis-document). For information on the correct use of the Andreasen method, see Gee and Bauder (1986).

Depending on the degree of accuracy and reproducibility required, some of the steps of the standard procedure below can be omitted. To decide which steps can be left out, the magnitude of the effect of each material-related parameter is provided in Table 6.5.1.

Standard sedimentary particle size analysis procedure for clays:

6.3.1. Divide the bulk-sample by means of a sample splitter, to ensure that the small sample (-s) to be analysed is representative of the whole. Before splitting, the bulk-sample must be ground, and thereafter homogenised by shaking and tumbling it for 1 min. in an irregular fashion. The latter is to ensure that smaller and larger particles and aggregates are not partially separated – as will happen during constant, uniform shaking (section 3.1).

6.3.2. Conduct the appropriate dissolution methods on each soil or soft sediment to be analysed, by using the method (-s) described in Kunze and Dixon (1986) (also see section 1.5.7.2). This is to destroy all aggregates, which might not be broken up by subsequent ultrasonic treatment. First, test which of the dissolution treatments is

necessary, and apply them as mild as possible.

6.3.3. Centrifugally wash once with distilled water to remove most of the dissolved ions left over after dissolution treatment. Facilitate retrieval of samples through flocculation by heating them to at least 80 °C just before each centrifugation. Conduct cation exchange with $CaCl_2$ or NaCl, followed by centrifugal washing with distilled water only until no Cl^- is detected with 0.01 M $AgNO_3$ (Klute, 1986). Alternatively, repeat the washing until the suspension conductivity is less than 0.6 mS/cm, which can be regarded as a negligible salt content (Herrera, 1999). However, when the smallest particles remains in suspension, reduce the pH of only the supernatant to 5.0 with a few drops of 0.001 M HCl, followed by re-heating to 80 °C just before centrifugation. This will aid flocculation sedimentation of the remaining suspension. The addition of salt to flocculate the clay should be omitted, since it will compromise accuracy of the subsequent particle size analysis (section 4.1.1). Alternatively, heated sample suspension can be desalinated by means of vacuum filtration, or dialysis can be employed.

6.3.4. If cation exchange is not conducted, centrifugally wash with distilled water anyway, to remove all soluble salts that might still be present in the clay. The latter is needed to facilitate complete dispersion during the subsequent particle size analysis. This is necessary despite the use of a deflocculant (section 4.1.1).

6.3.5. *Only if accurate results of clay mixtures are required*, remove a small portion of the wet clay and store the rest in a closed container. Conduct qualitative mineralogical analysis on it by means of XRD (Whittig and Allardice, 1986). This is used to determine how much of each clay type is present. The mass fractions of each clay constituent are needed in order to calculate the volume fraction of each, which in turn is used to calculate the accurate average density for the clay mixture (section 1.5.10, and step 6.3.9 below).

6.3.6. If samples are for some reason dried in an oven overnight (not recommended; section 4.1.1.1), temperatures should not exceed 95 °C to prevent potential change of the surface characteristics (Grim, 1962) from affecting subsequent deflocculation. Lightly grind the remaining larger samples to sugar-sized agglomerates in a mortar and pestle. If a rubber-coated pestle is not available, make sure that there is always a thick enough layer of clay between the hard surfaces of the implements, to keep the pestle from grinding through onto the surface of the mortar. This will prevent delamination of the

clay platelets along {001} cleavage planes. To also keep potential rotational breakage to a minimum, great care must be taken to rather grind softly with patience, than harder to shorten preparation time (section 4.1.3.1). Thereafter, soak the samples overnight to soften any agglomerates left over from the grinding of the dry sample (section 4.1.3.2).

6.3.7. Add enough 1 g/l Dispex to 1 g of each sample intended for particle size analysis, to obtain a 0.7% Dispex concentration, by using the following formula:

$$V_{Defl.} = \frac{10 \times m_{Clay} C_{Defl.}}{C_{Stoc.}}$$

with: C_{Stoc} the concentration of the deflocculant stock solution in g/l (mass deflocculant as supplied/litre), $C_{Defl.}$ the required concentration of the deflocculant (mass deflocculant as supplied to the mass clay), and m_{Clay} is the mass of clay (in grams) to be suspended. At a 0.41% by volume solid concentration, a 1 g/l stock solution is most convenient to give the required Dispex concentration at 0.7% (section 4.1.2.1)

Important note: the XRD analysis requires Mg^{2+} cation exchange to facilitate the optimum adsorption of glycerol (Whittig and Allardice, 1986). But, cation exchange is prevented by deflocculants, for the same reasons as the removal of interstitial Ca^{2+} from Ca-montmorillonite (Bundy *et al.*, 1972; section 1.5.8.2.2). Therefore, Mg^{2+} exchange cannot be done with a deflocculant present. This is the reason for the removal during step 6.3.5 of the small portion of clay for Mg^{2+} saturation for XRD analysis before Dispex is added.

6.3.8. Dilute the clay suspension with distilled water to between 0.41% and 1% by volume. The volume of liquid needed to dilute the sample is given by the following formula:

$$V_{H_2O} = \frac{m_{Clay} 100}{Solids\%} - m_{Clay} - V_{Defl.}$$

with V_{H_2O} the volume of distilled water to be added to obtain the required solid concentration, after the deflocculant stock solution ($V_{Defl.}$) was already added. If the sample is wet from the last centrifugal washing with distilled water, place its sample container of known dry mass on a scale, and add distilled water to obtain the following mass for the container already holding the sample of known dry mass and the deflocculant stock solution ($V_{Defl.}$):

$$Mass\ container = Mass\ Clay + V_{H_2O} + V_{Defl.} + Mass\ empty\ container$$

6.3.9. When analysing clay mixtures, calculate the average density from the densities of the

clay components which were identified by qualitative XRD analysis with the following formula (section 1.5.10):

$$\rho_{avg} = \rho_1 v_1 + \rho_2 v_2 + \rho_3 v_3 + ...$$

with v_n the volume fraction of each clay component calculated as follows from the mass (m) and density (ρ_n) of each component:

$$v_1 = \frac{\frac{m_1}{\rho_1}}{\frac{m_1}{\rho_1} + \frac{m_2}{\rho_2} + \frac{m_3}{\rho_3} + ...}$$

Use 3.00 g/cm^3 as the density for Ca-montmorillonite (section 1.5.8.2.2), 1.0337 g/cm^3 for Na-montmorillonite (section 1.5.8.4.2), 2.63 g/cm^3 as an average density for kaolinite, 2.75 g/cm^3 for illite, and 2.3 g/cm^3 for vermiculite (Deer *et.al.*, 1966).

6.3.10. With the clay density of a single clay is to be analysed (or with the average clay density of a mixture calculated under point 6.3.9), calculate the cell scan rate (Sedigraph) or sedimentation time (Andreasen method) for each clay, or clay mixture. Do it for each 0.1 °C rise in temperature over the whole of the expected temperature range of
30-45 °C of the Sedigraph (section 1.4.2). Use the sieve size in µm of step 6.3.13 as the D_{max} value when calculating scan rate. To save time while calculating this, the same table can be used over-and-over in Excel by just changing the calculated densities.

6.3.11. Use clean Dispex solution, at 0.7% in distilled water, to adjust the 0% settings just prior to every analysis (section 4.2.1.4).

6.3.12. Conduct a 3 min. ultrasonic treatment on all sample suspensions. This will ensure that all agglomerates, left over after chemical dissolution, are also destroyed (especially if samples was dried after the last centrifugal washing).

6.3.13. Wet-sieve the soil or the soft sediment through a 53 µm sieve with the help of a rubber policeman, and catch the washings through a large enough funnel to accommodate the sieve. This will ensure that most other soil minerals are removed, and that no particles larger than the maximum particle size for sedimentary particle size analysis is retained (49.6 µm – section 1.5.1.1.1).

6.3.14. Conduct each particle size analysis at the correct scan rates (or sedimentation times) as calculated above (step 6.3.10). If the Sedigraph 5000D is used: manually change the

scan rate with every 0.1 °C increase in temperature (the newer model Sedigraph does it automatically – section 3.1).

When analysing clays at the operating temperature of 35 °C of the Sedigraph, the particle size distribution must only be obtained down to a minimum particle size of 0.56 μm. Below 0.56 μm sedimentary particle size analysis results become increasingly inaccurate due to Brownian diffusion (section 1.5.1.1.2) – even at 1 μm, accuracy begins to suffer (see the error values of the Andreasen method, at 0.6% solids by volume, in Table 1.5.1.2.1).

6.3.15. Kaolinite suspensions, deflocculated with Dispex, can safely be stored for up to 9 weeks, and repeatedly be shaken up and re-analysed. With this treatment, there is no danger of hydrolysis or de-agglomeration compromising accuracy and repeatability (sections 4.2.3.1 and 4.2.3.2). Stored kaolinite suspensions do not, and should not be re-sonicated – shaking is effective enough to re-disperse them. In this way damage to clay particles due to ultrasonic aberration, and accompanying problems with repeatability and accuracy, can both be kept to a minimum.

However, if a clay suspension contains swell-clays, it needs to be analysed directly after ultrasonic treatment to prevent its decrease in particle size due to ageing (section 1.5.8.3.4).

6.3.16. If the Sedigraph 5000D is used, make sure that, apart from the prescribed procedures of the handbook, the measures to minimise the effects of apparatus-related parameters are all applied (section 3.1).

6.5 MAGNITUDE OF THE EFFECT OF EACH PARAMETER ON ACCURACY

To round off this report, the experimentally determined errors in cmp of each material-related parameter is summarised below in table form. Since all apparatus-parameters were kept constant, these errors only relates to the material, and are therefore applicable to all sedimentary methods. The Maximum Error of a parameter gives an indication of its effect on the *accuracy*, whereas the Error Variation indicates its effect on *reproducibility* and *repeatability*.

Table 6.5.1. Magnitude of the errors caused by material-related parameters

Parameter	**Maximum Error**	**Error Var.**	**Text Reference**
SAMPLE PREPARATION:			
Using organic dipoles during centrifugal washing without subsequent drying	0.2 – 1.6% cmp	1.4%	Section 4.1.1.1
Ethanol	3.1% cmp at 1 μm	1.8%	
Methanol	2.6% cmp at 2 μm	2.5%	
Acetone	4.6% cmp at 2 μm	4.6%	
Presence of soluble salts	≈ 0.0 – 5.6% cmp	≈ 5.6%	Section 4.1.1
No overnight soaking	1.0 – 4.5% cmp	3.5%	Section 4.1.3.2.1
pH not adjusted to 9.5	0.9 – 2.1% cmp at 1 μm	1.2%	Section 4.1.2.2
Grinding:			
Not ground before sonication:	-11.0 – 1.0% cmp	12%	Section 4.1.3.1
Too heavily ground before sonication:	1.0 – 6.0% cmp	5%	Section 4.1.3.1
No stirring during ultrasonic treatment	0.0% cmp		Section 4.1.3.3

Continued on next page

Table 6.5.1..Continued

Parameter	Maximum Error	Error Variation	Text Reference
PHYSICAL AND CHEMICAL PROPERTIES OF THE SUSPENSION:			
Using ρ of dist. water to calculate scan rate	0.0% cmp		Section 4.2.1.1.2
Using η of dist. water to calculate scan rate	0.0 – 5.78% cmp at 35 °C	5.78%	Section 4.2.1.3
Adjusting the 0% setting with dist. water:			
Using dist. water:	1.5% cmp		Section 4.2.1.4
Using deflocculant solution:	0.5% cmp		Section 4.2.1.4
SWELL-CLAYS, AND ITS MIXTURES:			
Variation when different deflocculants are used with Ca-montmorillonite	0.2 – 5.2% cmp	5%	Section 5.1
Inaccuracy of mixtures with illite, kaolinite, and Ca-montmorillonite	1.5 – 4.7% cmp	3.2%	Section 5.2

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